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PHOTOCHEMICAL MODEL

Report No 82-483-K

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ABSTRACT

Many reaction mechanisms have been developed to describe photochemical smog formation. These photochemical models are believed to be important tools for examining and understanding the fate of the atmospheric emissions from refineries, fossil fuel fired power plants, etc. This report reviews the chemistry of photochemical smog formation and some of the many models which have been reported to simulate its occurrence. The Carbon Bond Mechanism is recommended as a basis from which to develop a model capable of describing the chemistry of the emissions from Ontario Hydro's fossil fuel fired generating stations.

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To Mr. F.J. Kee
Director of Research

PHOTOCHEMICAL MODEL

1.0 INTRODUCTION

Photochemical smog is formed primarily as a result of a series of homogeneous gas phase reactions initiated when pollutants in the troposphere absorb the sun's radiation. The chemical species involved in these reactions include free radicals such as HO·, HO_2·, RO·, RO_2· and RCO_2·, and many trace molecular species, eg, NO, NO_2, CO, O_3, SO_2 and hydrocarbons. In recent years the mechanism of smog formation has been the subject of extensive research efforts. Attempts have been made to explain its production with a series of elementary chemical reactions. The kinetic mechanism can then be written in terms of a set of first order differential equations where the change in concentration of the reacting components, intermediates and products is expressed with respect to a change in time. Given the initial conditions and the rate constants for the elementary reactions involved, the computer can be used to generate, by a numerical solution, reactant and product concentration versus time curves. Photochemical smog formation can thereby be simulated and the impact of anthropogenic emissions on air quality can be evaluated. The set of reactions selected to describe smog formation is known as a photochemical model.

The goal of this study was to select/develop a photochemical model which can be used to simulate the reactions of the emissions from Ontario Hydro's fossil fuel fired generating stations. The model is one of many tools required to estimate Hydro's contribution to the production of photochemical smog and ensuing acid rain. It would provide a method with which to evaluate the effect of slight variations in the chemical composition of emissions on photochemical smog formation (ie, the effect of a decrease in SO_2 and/or NO_x concentrations). The report begins with a review of the chemical species and reactions involved in photochemical smog formation followed by an examination of the models which have been advanced to simulate its occurrence.

2.0 CHEMICAL SPECIES INVOLVED IN PHOTOCHEMICAL SMOG FORMATION

Very many chemical species are involved in the production of photochemical smog, the major reactants include HO·, NO_x, O_3, CO, SO_2 and hydrocarbons. NO_x, CO, SO_2 and hydrocarbons are found in the plumes emitted by fossil fuel fired power plants, refineries, etc. The emitted NO_x is predominantly NO (90-95%) and the remainder NO_2. The hydroxyl radical, ·OH, and ozone, O_3, are natural components of the atmosphere, however, in the presence of NO_x, CO, SO_2 and hydrocarbons, the concentrations of ·OH and O_3 vary dramatically. Photochemical smog formation is critically dependent upon the sun's radiation. This relationship is illustrated by the dependence of the extent of photochemical smog formation on hν, latitude, and temperature. Examination of the contribution of a particular chemical species to smog formation is difficult because of the dependence of the concentration and reactions of one reactant on the presence of many others. The hydroxyl radical provides the chief source and sink of many photochemical oxidants and is believed to be the most important chemical component in photochemical smog formation. The review of the chemistry of photochemical smog formation will therefore begin with an examination of the production of ·OH and its reactions with atmospheric pollutants.

2.1 Hydroxyl Radical (·OH)

The hydroxyl radical (·OH) is a very strong oxidant and through its chemical reactions may ultimately affect the climate, the pH of rain and stratospheric ozone levels. To illustrate: (i) reaction of ·OH with NO_2 and SO_2 yields HNO_3 and H_2SO_4, respectively, which are ultimately incorporated into rainwater resulting in the lowering of its pH;/1,2/ (ii) tropospheric ·OH oxidizes CH_3CCl_3, a widely used degreasing agent, thereby limiting its reaction with stratospheric ozone/2/. The concentration and distribution of tropospheric ·OH are dependent upon the abundance of many other atmospheric pollutants including H_2O, O_3, CH_4, CO, NO and NO_2/2/. All of these species, with the exception of CH_4, show significant variation with latitude, altitude and time.

In the troposphere, the primary source of OH radicals is the reaction of $O(^1D)$ with water, as shown in equation 2-1/3/.

$$O(^1D) + H_2O \rightarrow 2 \cdot OH \qquad (2\text{-}1)$$

$$k = 2.3 \times 10^{-10} \exp((0 \pm 50)/T),\ T = 200 - 300°K$$

The $O(^1D)$ atoms are generated by photolysis of O_3 between 3100 Å and the short wavelength limit of the tropospheric UV-B-radiation, equation 2-2.

$$O_3 + h\nu \ (\lambda \leq 3100 \text{ Å}) \rightarrow O(^1D) + O_2(^1\Delta_g) \qquad (2\text{-}2)$$

This is the most important photodissociation process for O_3 above 40 km/4/. Below 25 km, the level at which the maximum concentrations of O_3 occur, $O(^1D)$ is formed primarily from absorption of radiation in the region λ=3000 to 3100 Å. This is because radiation of wavelengths less than 3000 Å has been absorbed by other atmospheric species, eg, O_2, N_2, before it reaches the 25 km level. At wavelengths greater than 3102 Å there is insufficient electronic energy for the dissociation process and if it occurs, rotational-vibrational energy must be used, reactions 2-3 and 2-4/4/.

$$O_3 + h\nu \ (\lambda > 3102 \text{ Å}) \rightarrow O_2(^3\Sigma) + O(^1D) \qquad (2\text{-}3)$$

$$\rightarrow O(^3P) + O_2(^1\Delta_g \text{ or } ^1\Sigma) \qquad (2\text{-}4)$$

Above 40 km ($\lambda \leq 3100$ Å) $O(^1D)$ and $O_2(^1\Delta_g)$ are produced continuously, reaction 2-2, below 25 km the $O(^3D)$ production process is important, reaction 2-3, but it is less important than $O(^3P)$ production, reaction 2-4. Determination of the rate constants for reactions 2-2 to 2-4 is difficult due to the uncertainty in the quantum yield of $O(^1D)$ from the photolysis of O_3. At the earth's surface the rate constant for reaction 2-2 is believed to decrease rapidly as the product of the concentration of atmospheric ozone times the secant of the solar zenith angle increases. The solar zenith angle is the angle between the sun's rays and the perpendicular to the earth, eg, an overhead sun has a solar zenith angle of 0°. $O(^1D)$ can also be produced from the photodissociation of O_2 (λ <1750 Å). However, the photodissociation coefficient for this process becomes neglible below an altitude of about 85 km. For radiation λ>1750 Å there is insufficient energy to photodissociate O_2 to produce electronically-excited atoms/4/. Typical concentrations of $O(^1D)$ at various altitudes for an overhead sun are as follow/4/:

0 km	= 2.2×10^{-2}	molecules cm^{-3}
10 km	= $<10^{-1}$	molecules cm^{-3}
20 km	= 1	molecules cm^{-3}
50 km	= 600	molecules cm^{-3}

The concentration of $O(^1D)$ reaches a maximum at noon and the species disappears at night. The steady-state concentration of •OH varies directly with that of $O(^1D)$. As a result the maximum concentration of OH radicals is reached about noon and rapidly disappears after sundown. An average daylight concentration of •OH, for an overhead noonday sun and at an altitude of 20 km, is $(1.3 \pm 0.4) \times 10^6$ molecules cm^{-3} /4/. OH radical production from $O(^1D)$ and H_2O dominates in the tropics and subtropics. The lifetimes for $O(^1D)$ and O_3 are always less than 5000 s and the majority of $O(^1D)$ atoms produced are thermally quenched by air molecules, eg, O_2, typical concentration 0 to 20 km above the earth's surface = $3.6 \times 10^{17} - 5.3 \times 10^{18}$ molecules cm^{-3}; N_2, typical concentration 0 to 20 km above the earth's surface = $1.4 \times 10^{18} - 2.0 \times 10^{19}$ molecules cm^{-3}, reaction 2-5/4/.

$$O(^1D) + M \rightarrow O(^3P) + M \qquad (2\text{-}5)$$

$M = N_2$, $k = 5.4 \times 10^{-11}$ cm^3 s^{-1}, $T = 298°K$

$M = O_2$, $k = 7.4 \times 10^{-11}$ cm^3 s^{-1}, $T = 298°K$

•OH reacts rapidly with almost all other species present in the atmosphere, important reactions include:

$$\text{•OH} + CO \rightarrow CO_2 + H \qquad (2\text{-}6)$$

$k = 2.8 \times 10^{-13}$ cm^3 $molecule^{-1}s^{-1}$, $T = 298°K$, 1 atm P

$$\text{•OH} + NO_2 + M \rightarrow HNO_3 + M \qquad (2\text{-}7)$$

$M = N_2$ $k = (2.6 \pm 0.3) \times 10^{-30}$ $(T/300)^{-2.9 \pm 0.7}$

cm^6 $molecule^{-2}$ $s\text{-}1$,

$T = 200 - 300°K$

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$$k_\infty = (2.4 \pm 1.2) \times 10^{-11}(T/300)^{-1.3\pm1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$T = 200 - 300°K$$

$$\cdot OH + CH_4 \rightarrow CH_3 + H_2O \qquad (2\text{-}8)$$

$$k = 2.4 \times 10^{-12} \exp(-(1710 \pm 200)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1},$$

$$T = 200 - 300 °K$$

$$\cdot OH + HCl \rightarrow H_2O + Cl \qquad (2\text{-}9)$$

$$k = 2.8 \times 10^{-12} \exp(-(425 \pm 100)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$T = 200 - 300°K$$

$$\cdot OH + HO_2\cdot \rightarrow H_2O + O_2 \qquad (2\text{-}10)$$

$$k = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2\cdot \qquad (2\text{-}11)$$

$$k = 1 \times 10^{-11} \exp(-(750 \pm 350)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$T = 200 - 300°K$$

$$2 \cdot OH \rightarrow H_2O + O(^3P) \qquad (2\text{-}12)$$

$$k = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \; T = 300°K$$

$$\cdot OH + O_3 \rightarrow HO_2\cdot + O_2 \qquad (2\text{-}13)$$

$$k = 1.8 \times 10^{-12} \exp(-930/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$T = 238 - 357°K$$

Reaction of ·OH with carbon monoxide (CO), equation 2-6, is the primary removal path for atmospheric CO/1/. The production of H atoms from this reaction leads to the formation of $HO_2\cdot$ and H_2O_2 as described in reactions 2-14 and 2-15. ·OH is eventually regenerated via reactions 2-16 to 2-18. $HO_2\cdot$ and H_2O_2 are very important for controlling tropospheric ·OH levels, reactions 2-15 to 2-19.

$$H + O_2 + M \rightarrow HO_2\cdot + M \qquad (2\text{-}14)$$

$M = N_2$, $k = (5.5 \pm 0.5) \times 10^{-32} (T/300)^{-1.4\pm0.5}$ cm^6 $molecule^{-2}$ s^{-1},

$T = 200 - 300°K$

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2 \quad k = 2.5 \times 10^{-12} \qquad (2\text{-}15)$$

cm^3 $molecule^{-1}$ s^{-1}, $T = 298°K$

$$HO_2\cdot + NO \rightarrow \cdot OH + NO_2 \qquad (2\text{-}16)$$

$k = 8.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, $T = 298°K$

$$HO_2\cdot + O_3 \rightarrow \cdot OH + 2O_2 \qquad (2\text{-}17)$$

$k = (1.4 \pm 0.4) \times 10^{-14} \exp(-(580 \pm 100)/T)$ $cm^3 molecule^{-1}$ s^{-1}, $T = 250 - 370°K$

$$HO_2\cdot + O(^3P) \rightarrow \cdot OH + O_2 \qquad (2\text{-}18)$$

$k = 3.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, $T = 298°K$

$$H_2O_2 + h\nu \rightarrow 2 \cdot OH \qquad (2\text{-}19)$$

$$H_2O_2 \rightarrow \text{heterogeneous removal (chain termination)} \qquad (2\text{-}20)$$

The cycling of $HO_2\cdot$ to $\cdot OH$ is especially important at high latitudes and altitudes, and at high concentrations of NO. The $\cdot OH$ distribution is generally insensitive to the rate assumed for heterogeneous loss. Studies by Chameides and Tan/1/ suggested that the relative abundances of $\cdot OH$ and $HO_2\cdot$ are dependent upon the relative rates of reactions 2-1, 2-6, 2-16 and 2-17, and may be approximated by equation 2-21.

$$\frac{n(HO_2\cdot)}{n(\cdot OH)} \sim \frac{n(CO)k_{(2\text{-}6)}}{n(NO)k_{(2\text{-}16)} + n(O_3)k_{(2\text{-}17)}}, \qquad (2\text{-}21)$$

where n represents the number density of the appropriate species. Because $n(HO_2\cdot)/n(\cdot OH)$ is typically of the order of 10^2, significant enhancements in $\cdot OH$ concentration can result from an increase in the rate of $\cdot OH$ regeneration from $HO_2\cdot$ even if primary production of free radicals from $O(^1D) + H_2O$ does not increase/1/. Reaction of methane (CH_4) with $\cdot OH$, equation 2-8, initiates a series of reactions referred to as the methane oxidation chain and results in the generation of H_2, H_2CO and CO/1/. Reactions which make up this sequence include:

$$CH_3O_2\cdot + HO_2\cdot \rightarrow CH_3OOH + O_2 \qquad (2\text{-}22)$$

$$k = 7.7 \times 10^{-14} \exp(1296/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$T = 274 - 338°K$$

$$CH_3OOH + \cdot OH \rightarrow CH_3O_2\cdot + H_2O \rightarrow \text{products} \qquad (2\text{-}23)$$

$$k = 1 \times 10^{-11} \exp(-(750 \pm 350)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$T = 200 - 300°K$$

$$CH_3O_2\cdot + CH_3O_2\cdot \rightarrow 2CH_3O\cdot + O_2 \qquad (2\text{-}24)$$

$$k = (1.6 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\cdot OH + CH_3O_2\cdot \rightarrow CH_3O\cdot + HO_2\cdot \qquad (2\text{-}25)$$

$$CH_3OOH + h\nu \rightarrow CH_3O\cdot + \cdot OH \qquad (2\text{-}26)$$

$$H_2CO + \cdot OH \rightarrow HCO\cdot + H_2O \qquad (2\text{-}27)$$

$$k = 1.0 \times 10^{-11} \exp((0 \pm 200)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$T = 200 - 300°K$$

$$H_2CO + h\nu \rightarrow HCO + H \qquad (2\text{-}28)$$

$$H_2CO + h\nu \rightarrow CO + H_2 \qquad (2\text{-}29)$$

As will be seen in later sections, the products of these reactions have a large impact upon the concentrations of other atmospheric pollutants in addition to their effect on $\cdot OH$ levels. Unfortunately, many of the rate constants are not well known.

Near sunset, the concentration of the OH radical decreases rapidly as reactions 2-1, 2-2 and 2-19 become negligible. At night $HO_2\cdot$ and $\cdot OH$ are cycled by reactions 2-6, 2-14, 2-17 and by the methane oxidation sequence. The concentrations of $\cdot OH$ and $HO_2\cdot$ slowly decrease due to the formation of H_2O_2 and CH_3OOH, and their subsequent heterogeneous removal, equations 2-15, 2-20 and 2-22.

2.2 Ozone (O_3)

Ozone is a strong oxidant produced in the atmosphere via photochemical oxidation. It is uncertain what fraction of the ozone present in the lower boundary layer is the product of photochemical processes and how much is due to injection from higher atmospheric layers as a result of atmospheric motions. The ozone concentration varies with season, temperature and cloud cover. Background levels of O_3 normally vary between 0.01 and

0.03 ppm with an average value of 0.025 ppm (6×10^{11} molecules cm^{-3})/4/. The levels of ozone present in the lower atmosphere are also dependent upon a complicated cycle of reactions involving NO, NO_2 and hydrocarbons.

The only O_3 producing reaction in the atmosphere is described in equation 2-30.

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (2\text{-}30)$$

$M = N_2$, $k = (6.2 \pm 0.9) \times 10^{-34} (T/300)^{-2.0 \pm 0.5}$

cm^6 molecule^{-2} s^{-1}

$T = 220 - 300°K$

$M = O_2$, $k = (6.9 \pm 1.0) \times 10^{-34} (T/300)^{-1.25 \pm 0.2}$

cm^6 molecule^{-2} s^{-1}

$T = 219 - 368°K$

One source of the $O(^3P)$ consumed in reaction 2-30 is the photolysis of NO_2.

$$NO_2 + h\nu \ (\lambda \leq 3979 Å) \rightarrow NO + O(^3P) \qquad (2\text{-}31)$$

$\lambda = 3980$ Å, $\Phi = 0.72$ (quantum yield)

The nitric oxide (NO) formed in 2-31 reacts with ozone to produce NO_2 via reaction 2-32. The cycle is summarized in Figure 2.1.

(2-32)

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$k = (2.34 \pm 0.23) \times 10^{-12} \exp(-(1450 \pm 50/T)\ cm^3\ molecule^{-1}\ s^{-1},$$

$$T = 203 - 361°K$$

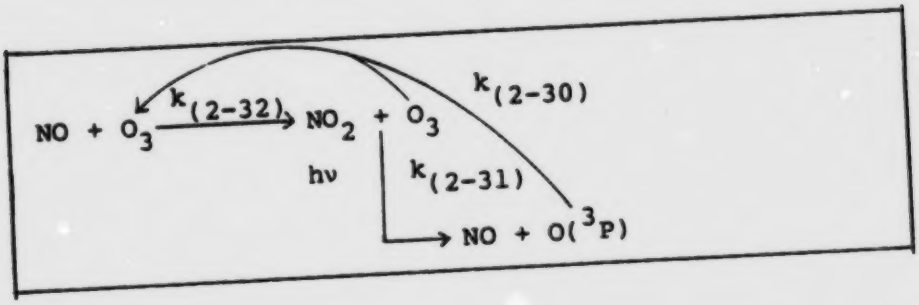


Figure 2.1 The $NO/NO_2/O_3$ cycle.

Reactions 2-30 and 2-31 result in the production of O_3, reaction 2-32 destroys it. The concentraion of O_3 is critically dependent upon how fast NO is converted to NO_2. $[O_3]$ can be expressed as a ratio of $[NO_2]$ to [NO]/5/:

$$[O_3] = \frac{\phi k_{(2-31)} [NO_2]}{k_{(2-32)} [NO]}$$, where $\phi k_{(2-31)}$ and $k_{(2-32)}$ are

the rate constants for reactions 2-31 and 2-32, respectively. When the concentration of NO becomes very small in a mixture containing significant amounts of NO_2, ozone appears in significant quantities in the air. Reactions 2-33 and 2-34 compete with 2-30 for oxygen atoms, but the rates at which these reactions proceed are orders of magnitude slower than the rate of reaction 2-30.

$$O(^3P) + NO + M \rightarrow NO_2 + M \qquad (2\text{-}33)$$

$M = N_2$, $k = 1.55 \times 10^{-32} \exp(584/T)$ cm^6 $molecule^{-2}$ s^{-1},

$T = 220 - 500°K$

$$O(^3P) + NO_2 \rightarrow NO + O_2 \qquad (2\text{-}34)$$

$k = 9.1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, $T = 230\text{-}339°K$

The conversion of NO to NO_2 is accelerated in the presence of hydrocarbons. Hydrocarbons react with atomic O, O_3 and $\cdot OH$ to produce oxygenated radicals (eg, $HO_2\cdot$, $RO_2\cdot$ and $RCO_3\cdot$), reactions 2-35 to 2-39, which convert NO to NO_2 via reactions 2-40 to 2-42/5/.

$$HC \xrightarrow{O} HO_2\cdot + RO_2\cdot + CO \qquad (2\text{-}35)$$

$$\rightarrow RCO_3\cdot + RO_2\cdot \qquad (2\text{-}36)$$

$$HC \xrightarrow{O_3} RO\cdot + HO_2 + CO + \text{aldehydes} \qquad (2\text{-}37)$$

$$\xrightarrow{O_3} \text{aldehyde} + H_2O + CO \qquad (2\text{-}38)$$

$$HC \xrightarrow{\cdot OH} RO_2\cdot + \text{aldehyde} \qquad (2\text{-}39)$$

(HC represents hydrocarbons, R is an alkyl group.)

$$HO_2\cdot + NO \rightarrow NO_2 + \cdot OH \qquad (2\text{-}40)$$

$$RO_2\cdot + NO \rightarrow NO_2 + RO\cdot \qquad (2\text{-}41)$$

$$RCO_3\cdot + NO \rightarrow NO_2 + RCO_2\cdot \qquad (2\text{-}42)$$

$HO_2\cdot$ and $RO_2\cdot$ are regenerated via reactions 2-43 and 2-44.

$$RO\cdot + O_2 \rightarrow HO_2\cdot + \text{aldehyde} \qquad (2\text{-}43)$$

$$RCO_2\cdot + O_2 \rightarrow RO_2\cdot + CO_2 \qquad (2\text{-}44)$$

As the hydrocarbon concentration increases, more oxygenated radicals will be formed which convert NO to NO_2. Increases in the concentration of NO_2 result in increases in the concentration of O_3. When the ratio of hydrocarbons to nitrogen oxides is low, as is the case in urban areas, increasing [NO] results in reduced levels of ozone. But, when the system is deficient of NO, ie, [HC]:[NO] is high, addition of NO results in an increase in O_3 formation. This is presumably due to the conversion of all NO to NO_2. The ratio at which the effect of NO reverses is unclear but it appears to be a function of the hydrocarbon. To illustrate, Sickles et al/5/ in 1977 reported that the critical ratio, [HC]:[NO], was about 20 parts C per part NO_x when the hydrocarbon present was isopentane. Hamming et al/5/ reported a critical ratio of about 5 parts C per part NO_x in the irradiation of more reactive HC's such as those found in automobile exhaust. Studies reported by Miller et al/6/ in 1978 suggested that maximum concentrations of ozone are attained when the ratio of nonmethane hydrocarbons to NO_x is approximately 8:1.

These results suggest that the more reactive the hydrocarbons are, the smaller the critical ratio where the role of NO is reversed. The strong dependence of the concentration of O_3 on the levels of NO and NO_2 has a great impact on the concentrations of O_3 detected in power plant plumes. Relatively close to the source the level of NO is high and the concentration of O_3 in the plume is lower than the O_3 levels detected in background air. This deficit is due to the rapid reaction of NO with the O_3 of the background air trapped in the plume. As the plume disperses and moves downwind, more background air containing O_3, HC's, etc, is entrained into the plume and NO is rapidly oxidized to NO_2 resulting in a gradual increase in the level of O_3. In many power plant plume studies O_3 "bulges", or regions with concentrations of O_3 much higher than the levels detected in ambient air, have been observed at points very far downwind of the stacks.

In addition to the reaction of O_3 with NO, O_3 reacts with NO_2 to give NO_3, equation 2-45.

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \qquad (2\text{-}45)$$

$$k = (1.34 \pm 0.11) \times 10^{-13} \exp(-2466 \pm 30/T)$$

$$cm^3\ molecule^{-1}\ s^{-1}$$

$$T = 231\text{-}298°K$$

Reaction of O_3 with NH_3 results in a complicated series of reactions, the overall stoichiometry of which is given in equation 2-46/4/.

$$2NH_3 + 4\ O_3 \rightarrow 4\ O_2 + H_2O + NH_4NO_3 \qquad (2\text{-}46)$$

The sequence of reactions involved is as follows:

$$NH_3 + O_3 \rightarrow NH_3^+O_3^- \rightarrow NH_2 + \cdot OH + O_2 \qquad (2\text{-}47)$$

$$\cdot OH + NH_3 \rightarrow H_2O + NH_2 \qquad (2\text{-}48)$$

$$NH_2 + O_3 \rightarrow NH_2O + O_2 \qquad (2\text{-}49)$$

$$NH_2O + O_3 \rightarrow \cdot OH + O_2 + HNO \qquad (2\text{-}50)$$

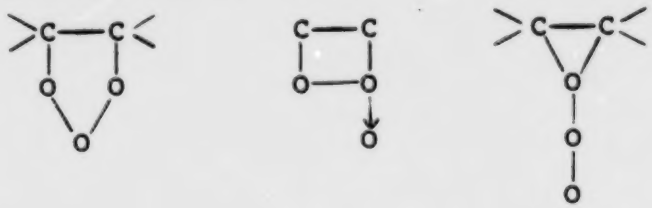
$$HNO + 2\ O_3 \rightarrow HNO_3 + 2\ O_2 \qquad (2\text{-}51)$$

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \qquad (2\text{-}52)$$

O_3 reacts with hydrocarbons to produce a number of products including aldehydes, H_2O and CO, these reactions were described by equations 2-37 and 2-38. Reaction of O_3 with alkenes is believed to proceed via the Criegee mechanism, equation 2-53/4/.

$$O_3 + R_1R_2C{=}{=}CR_3R_4 \rightarrow R_1R_2C{=}{=}O + R_3R_4COO \qquad (2\text{-}53)$$

where R_1, R_2, R_3 and R_4 represent hydrocarbon (or H) radical fragments. The reaction is thought to pass through one or more of the following intermediates:



I II III

A compound of structure I has been trapped at low T in the condensed phase and identified by NMR and ir spectra. The structure of R_3R_4COO is considered to be intermediate between the diradical IV and the zwitterion formulation V.

IV V

In the liquid phase R_3R_4COO is believed to react with aldehydes, ketones, itself or the solvent to generate a variety of products/4/. Examples of the unusual structures of the products of such reactions are listed in Figure 2.2.

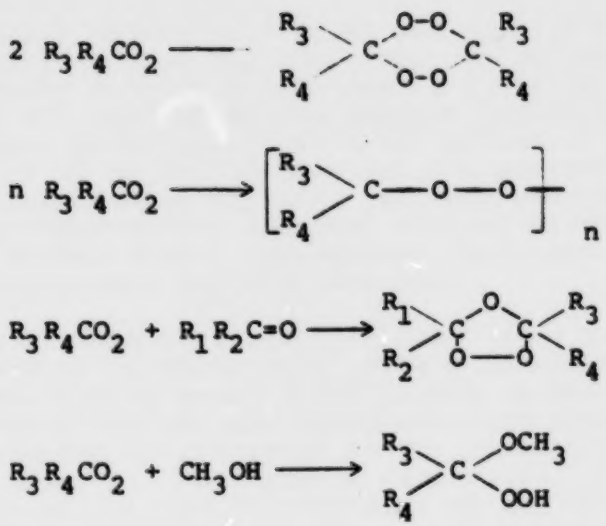
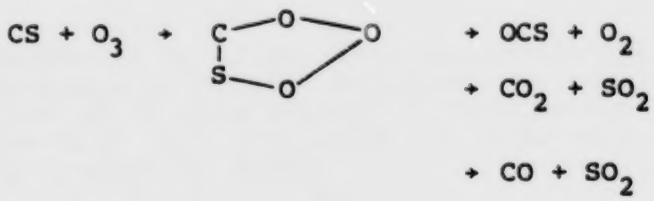


Figure 2.2 Selected reactions of the Criegee intermediate R_3R_4COO/4/

Reaction of O_3 with aromatic rings produces π-complexes, the interaction is however completely reversible and no net reaction has ever been measured.

O_3 reacts with CS as shown in equation 2-54.



(2-54)

2.3 Oxides of Nitrogen (NO_x)

NO_x represents the oxides of nitrogen. Members of this group include NO, NO_2, NO_3, N_2O_5, HNO_2 and HNO_3/4/. HNO_2 and HNO_3 are included because they rapidly interconvert with the other oxides of nitrogen. N_2O, the dominant oxide of nitrogen at the surface of the earth, is not a member but will be discussed later. When used in the context of air pollution chemistry, the term NO_x

generally refers only to NO and NO_2. The worldwide ambient concentration of NO_x ($NO + NO_2$) is believed to be 7.5×10^{10} molecules cm^{-3} (3×10^{-3} ppm)/4/. It is estimated that 500×10^6 tons of NO are emitted worldwide each year from natural sources, principally bacterial action. In addition, man-made sources of NO and NO_2 account for another 53×10^6 tons/yr of NO_x (computed as NO_2)/4/. Primary sources of manmade emissions of nitrogen oxides are coal and petroleum product combustion. On a global scale, the manmade contribution to NO_x production is significant but not dominant.

The most important reaction associated with the NO_x system is conversion of NO to NO_2. Ninety to ninety-five percent of the NO_x emitted by power plant plumes is NO, the remainder NO_2. In the first few seconds after emission approximately 2 to 7% of the NO released is converted to NO_2 by thermal reactions, equation 2-55/7/. The rate of conversion is proportional to the square of the concentration of NO and drops off dramatically as the plume is diluted. Generally, reaction 2-55 is important only when the concentration of NO is greater than 50 ppm.

$$NO + NO + O_2 \rightarrow 2\ NO_2 \qquad (2\text{-}55)$$

$$k = 3.3 \times 10^{-39} \exp(530/T)\ cm^6\ molecule^{-2}\ s^{-1},$$

$$T = 273 - 660°K$$

Conversion of NO to NO_2 also occurs via the following routes: (i) reaction of NO with entrained O_3, equation 2-32; (ii) reaction of NO with oxygenated hydrocarbon radicals, see Section 2.2; and (iii) reaction of NO with peroxy radicals such as $HO_2\cdot$, equation 2-40.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (2\text{-}32)$$

$$k = (2.34 \pm 0.23) \times 10^{-12} \exp(-1450 \pm 50/T)\ cm^3\ molecule^{-1} s^{-1},$$

$$T = 203 - 261°K$$

$$NO + HO_2\cdot \rightarrow NO_2 + \cdot OH \qquad (2\text{-}40)$$

$k = 3.3 \times 10^{-12} \exp(254/T)$ cm^3 $molecule^{-1}$ s^{-1},

$T = 230 - 400°K$

Reaction of nitric oxide, NO, with the hydroxyl radical yields HNO_2, equation 2-56, which reacts further with $\cdot OH$ to give NO_2, reaction 2-57.

$$NO + \cdot OH + M \rightarrow HNO_2 + M \qquad (2\text{-}56)$$

$M = N_2$, $k = (6.7 \pm 1.2) \times 10^{-31} (T/300)^{-3.3 \pm 1}$ cm^6

$molecule^{-2}$ s^{-1},

$T = 200 - 300°K$

$$HNO_2 + \cdot OH \rightarrow NO_2 + H_2O \qquad (2\text{-}57)$$

$k = 6.6 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, $T = 296°K$

Plumes containing significant levels of NO_2 appear yellow or brown in colour due to the absorption of blue light by NO_2.

After a high concentration of NO_2 has built up by means of reactions 2-32, 2-40 and 2-55 to 2-57, other reactions involving NO_2 become competitive and NO_2 is further oxidized. To illustrate:

$$NO + NO_2 + H_2O \rightleftharpoons 2\ HNO_2 \qquad (2\text{-}58)$$

$k = 6.0 \times 10^{-38}$ cm^6 $molecule^{-2}$ s^{-1}, $T = 296°K$

$$HNO_2 + h\nu \rightarrow NO + \cdot OH \qquad (2\text{-}59)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (2\text{-}45)$$

$k = (1.34 \pm 0.11) \times 10^{-13} \exp(-2466 \pm 30/T)$ cm^3 molecule^{-1} s^{-1},

$T = 291 - 298°K$

$$NO_2 + O + M \rightarrow NO_3 + M \qquad (2\text{-}60)$$

$M = N_2$, $k = 8.2 \times 10^{-32}$ cm^6 molecule^{-2} s^{-1}, $T = 297°K$

$$NO_3 + NO \rightarrow 2NO_2 \qquad (2\text{-}61)$$

$k = (1.9 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $T = 300°K$

$$NO_3 + NO_2 + M \rightleftharpoons N_2O_5 + M \qquad (2\text{-}62)$$

When the concentration of NO_2 exceeds that of NO, conversion of NO_3 and NO_2 to N_2O_5, reaction 2-62, predominates over reaction 2-61/7/. Hydrolysis of N_2O_5 yields nitric acid, equation 2-63.

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (2\text{-}63)$$

$k < 1.3 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1}, $T = 298°K$

Nitric acid is also produced via reaction of NO_2 with the hydroxyl radical, equation 2-64.

$$NO_2 + \cdot OH + M \rightarrow HNO_3 + M \qquad (2\text{-}64)$$

$M = N_2$, $k = (2.6 \pm 0.3) \times 10^{-30} (T/300)^{-2.9 \pm 0.7}$ cm^6 $molecule^{-2}$ s^{-1},

$T = 200 - 300°K$

Reaction of NO_2 with $HO_2\cdot$ yields peroxynitric acid, HO_2NO_2, which quickly decomposes back to starting materials.

Reaction of NO_2 with the hydrocarbon radical $RCO_3\cdot$ yields peroxynitrates of which peroxyacetyl nitrate (PAN) is the most prevalent. Peroxynitrates are generally strong oxidants.

$$RCO_3\cdot + NO_2 \rightleftharpoons RCO_3NO_2 \quad (R = CH_3, CH_3CH_2CH_2, C_6H_5) \qquad (2\text{-}65)$$

Other reactions of NO_x include:

$$RO_2\cdot + NO_2 \rightleftharpoons RO_2NO_2 \qquad (2\text{-}66)$$

$$RO\cdot + NO \underset{h\nu}{\rightleftharpoons} RONO \qquad (2\text{-}67)$$

Ammonia, NH_3, present in trace concentrations (~0.1 - 1 ppb) has the potential to play an important role in the neutralization of acids via reaction 2-68.

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \qquad (2\text{-}68)$$

The rate for this reaction is not, however, well established.

N_2O, the dominant oxide of nitrogen at the surface of the earth, is the waste product of life on earth. It is brought into the atmosphere through upward diffusion. The concentration of N_2O in the atmosphere therefore drops with increasing altitude until it becomes unimportant in the mesosphere. There are no chemical or photochemical sources of N_2O in the atmosphere, only removal mechanisms. Removal occurs predominantly by photodissociation, reaction 2-69, with some contribution from 2-70.

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \qquad (2\text{-}69)$$

$$O(^1D) + N_2O \rightarrow N_2 + O_2 \qquad (2\text{-}70)$$

$$\rightarrow 2NO$$

N_2O photodissociation extends to wavelengths of 3150Å, but most of the photodissociation in the upper stratosphere occurs at wavelengths <2500Å. Throughout the whole stratosphere, the loss via reaction 2-70 is only about 4% of that estimated for photodissociation. It is estimated about 98% of the N_2O introduced into the atmosphere is converted to N_2 and about 2% is converted to NO/4/.

2.4 Sulfur Dioxide (SO_2)

The only known natural source of SO_2 emissions is volcanic eruptions. The primary anthropogenic processes resulting in the release of SO_2 are the combustion of fossil fuels, the refining of petroleum, the smelting of ores containing sulfur and the manufacture of H_2SO_4/4/. Recent papers have examined the formation of SO_2 in the atmosphere as a result of the oxidation of H_2S, COS, CS_2 and CH_3SCH_3 (DMS)/8,9/. H_2S is a major product of plant and animal decay. Sze and Ko/8/ estimated that the oxidation of COS and CS_2, initiated by reaction with ·OH, could result in the production of about 8-12 Tg(S)/yr of SO_2. Although this source is relatively insignificant when compared to man-made contributions on a local scale, it can account for much of the SO_2 observed in the remote troposphere and stratosphere.

SO_2 absorbs light within the UV region of the solar radiation incident within the troposphere, that is, within the long wavelength tail of the relatively strong "allowed" band of SO_2 (2900-3000 Å) and within the weaker "forbidden" band in the 3400-4000 Å region. However, SO_2 photodissociation is energetically possible only when λ<2180 Å, reaction 2-71/10/.

$$SO_2 + h\nu \ (\lambda<2180 \text{ Å}) \rightarrow O(^3P) + SO \ (^3\xi^-) \qquad (2\text{-}71)$$

As a result, solar radiation absorbed by SO_2 within the troposphere leads to nondissociative, excited states of SO_2, reactions 2-72 to 2-74.

$$SO_2\ (\tilde{X}^1A_1) + h\nu\ (3400 < \lambda < 4000\text{Å}) \rightarrow SO_2\ (^3B_1) \qquad (2\text{-}72)$$

$$SO_2\ (\tilde{X}^1A_1) + h\nu\ (2400 < \lambda < 3300\text{Å}) \rightarrow SO_2\ (^1A_2) + \qquad (2\text{-}73)$$

(very short-lived)

$SO_2\ (^1B_1)$

(very long-lived)

The products of reaction 2-73, $SO_2\ (^1A_2)$ and $SO_2\ (^1B_1)$, are rapidly quenched by collision with major atmospheric gases, NO, O_2, equation 2-74. The primary product of the quenching reaction is the reactive $SO_2\ (^3B_1)$ molecule.

$$SO_2\ (^1A_2, {}^1B_1) + M \rightarrow SO_2\ (^3B_1) + M \qquad (2\text{-}74)$$

The $SO_2\ (^3B_1)$ molecule appears to be the major photochemically-active species formed in the photoexcitation of SO_2.

$SO_2\ (^3B_1)$ reacts with a number of reactive species present in the atmosphere, including O_2 and SO_2. Reaction of $SO_2\ (^3B_1)$ with O_2 leads to a transfer of energy from SO_2 to O_2 and the generation of excited singlet oxygen species, equations 2-75, 2-76.

$$SO_2\ (^3B_1) + O_2\ (^3\Sigma^-g) \rightarrow SO_2\ (\tilde{X}^1A_1) + O_2\ (^1\xi_g^+) \qquad (2\text{-}75)$$

$$\rightarrow SO_2\ (\tilde{X}^1A_1) + O_2\ (^1\Delta_g) \qquad (2\text{-}76)$$

The rate constant for the quenching of $SO_2\ (^3B_1)$ by O_2 (reaction 2-75 + reaction 2-76) is 1.6×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. Other products of this reaction include SO_3 and O_3, as described by equations 2-77 and 2-78.

$$SO_2\ (^3B_1) + O_2\ (^3\xi^-_g) \rightarrow SO_4\ (\text{cyclic}) \xrightarrow{O_2} SO_3 + O_3 \qquad (2\text{-}77)$$

$$SO_2\ (^3B_1) + O_2\ (^3\xi^-_g) \rightarrow SO_3 + O\ (^3P) \qquad (2\text{-}78)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (2\text{-}30)$$

The sum of the rate constants for reactions 2-77 and 2-78 is 3×10^{-15} cm^3 molecule^{-1} s^{-1}. The major chemical effect of SO_2 photoxidation by sunlight within the polluted atmosphere therefore appears to be generation of O_2 ($^1\xi_g^+$) and O_2 ($^1\Delta_g$) via reactions 2-75 and 2-76. Although the expected rates of reaction are relatively large, they are about 1/20th of those expected from reaction of excited NO_2 with O_2 when NO_2 and SO_2 are at comparable levels.

Reaction of SO_2 ($^3B_1$) with SO_2 yields SO_3, equation 2-79.

$$SO_2\ (^3B_1) + SO_2 \rightarrow SO_3 + SO\ (^3\Sigma^-) \qquad (2\text{-}79)$$

$$k = 7.0 \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

Reaction of SO_2 ($^3B_1$) with unreactive gases such as N_2, Ar, CO_2 and H_2O, results in quenching and no net chemical change.

The dominant paths for the oxidation of ground state SO_2 are reactions with $\cdot OH$, $HO_2\cdot$ and $CH_3O_2\cdot$, equations 2-80, 2-81 and 2-82, respectively.

$$\cdot OH + SO_2 + M \rightarrow HOSO_2\cdot + M \qquad (2\text{-}80)$$

$$k = (1.1 \pm 0.3) \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},\ T = 298°K,\ 1\ \text{atm air}$$

$$HO_2\cdot + SO_2 \rightarrow \cdot OH + SO_3 \xrightarrow{H_2O} H_2SO_4 \qquad (2\text{-}81)$$

$$k < 2 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},\ T = 298°K,\ 1\ \text{atm P}$$

$$CH_3O_2\cdot + SO_2 \rightarrow CH_3O\cdot + SO_3 \xrightarrow{H_2O} H_2SO_4 \qquad (2\text{-}82)$$

$k = (1.4\pm0.2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, T = 298°K, 1 atm P

Much experimental effort has been expended on the measurement of the rates of these reactions and many rate constants have been reported. Laboratory studies of SO_2 oxidation via reaction 2-80 suggest that the rate is dependent upon the nature of M, the pressure and the temperature. Calvert/11/ proposed the following relationship between the rate constant, hydroxyl radical concentration and temperature:

$$\text{Rate } SO_2 \text{ oxidation via 2-80} = [\cdot OH](1.06\times10^{-8}e^{1080/T})\%h^{-1} \qquad (2\text{-}83)$$

Typical values estimated for ·OH concentrations in a hydrocarbon-nitric oxide polluted lower troposphere, at 40°N latitude, reach a maximum of about 9×10^6 molecule cm^{-3} for summer noontime and about 2.4×10^6 molecule cm^{-3} in winter. The rate of SO_2 oxidation can therefore be calculated to be as high as 3.6% h^{-1} at 1200 h in summer and about 1% h^{-1} in winter/11/.

In polluted atmospheres, Calvert/10/ has also suggested that the rate of SO_2 oxidation shows equivalent contributions from hydroxyl, hydroperoxyl ($HO_2\cdot$) and methylperoxyl ($CH_3O_2\cdot$) radicals. However, experimental determinations of the reaction rate constants of SO_2 with $HO_2\cdot$ (reaction 2-81)/12,13/ and SO_2 with $CH_3O_2\cdot$ (reaction 2-82)/14/ are not well established and the contributions of $HO_2\cdot$ and $CH_3O_2\cdot$ to the oxidation of SO_2 in the atmosphere must be considered as questionable. The rates of reaction of SO_2 with other organic peroxy radicals, such as butylperoxy radicals, are approximately 10^{-4} to 10^{-5} times that with $CH_3O_2\cdot$, and these reactions are not generally considered.

SO_2 can also be oxidized by singlet oxygen, $O(^3P)$, as described in equation 2-84.

$$O(^3P) + SO_2 \ (+M) \rightarrow SO_3 \ (+M) \qquad (2\text{-}84)$$

$M = N_2/O_2$, $k = (5.7\pm0.5) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1},

T = 298°K, 1 atm P

However, for the normal conditions encountered in the lower troposphere it is generally estimated that less than 0.01% h^{-1} oxidation of SO_2 can occur from this reaction/11/. The hydroxyl radical therefore appears to dominate the rate of SO_2 oxidation in the atmosphere.

The $HOSO_2$ radical formed from reaction of $\cdot OH$ with SO_2, equation 2-80, is not stable and can be further oxidized, reactions include:

$$HOSO_2\cdot + O_2 \rightarrow HOSO_2OO\cdot \qquad (2\text{-}85)$$

$$HOSO_2\cdot + O_2 \rightarrow HO_2\cdot + SO_3 \qquad (2\text{-}86)$$

Reaction 2-86 is endothermic and is not expected to compete with 2-85 which is exothermic. The radical $HOSO_2OO\cdot$ will oxidize NO to NO_2 and NO_2 to NO_3, equations 2-87 to 2-89.

$$HOSO_2OO\cdot \xrightarrow{NO} HOSO_2O\cdot + NO_2 \qquad (2\text{-}87)$$

$$HOSO_2OO\cdot \xrightarrow{NO_2} HOSO_2OONO_2 \qquad (2\text{-}88)$$

(inorganic analogue to PAN)

$$HOSO_2OO\cdot \xrightarrow{NO_2} HOSO_2O\cdot + NO_3 \qquad (2\text{-}89)$$

Other reactions of $HOSO_2OO\cdot$ are described by equations 2-90 and 2-91.

$$HOSO_2OO\cdot \xrightarrow{HO_2\cdot} HOSO_2O_2H + O_2 \qquad (2\text{-}90)$$

$$HOSO_2OO\cdot + HOSO_2OO\cdot \rightarrow 2\ HOSO_2O\cdot + O_2 \qquad (2\text{-}91)$$

The $HOSO_2O$ radical produced in the above reactions can abstract H from hydrocarbons, aldehydes or other hydrogen containing species

to yield H_2SO_4. $HOSO_2O\cdot$ may also add to alkenes to generate organic sulfate. Reaction of $HOSO_2O\cdot$ with NO and NO_2 yields nitrosyl sulfuric acid, $HOSO_2ONO$, and nitrylsulfuric acid, $HOSO_2ONO_2$, respectively, equations 2-92 and 2-93.

$$HOSO_2O\cdot \xrightarrow{NO} HOSO_2ONO \xrightarrow{\text{aerosol } (H_2O)} HONO + H_2SO_4 \qquad (2\text{-}92)$$

$$HOSO_2O\cdot \xrightarrow{NO_2} HOSO_2ONO_2 \xrightarrow{\text{aerosol } (H_2O)} HONO_2 + H_2SO_4 \qquad (2\text{-}93)$$

The assignment of rate constants for reactions 2-90 to 2-93 is speculative, but once $\cdot OH$ has added to SO_2, the subsequent reactions proceed rapidly to form H_2SO_4, peroxysulfuric acid and other compounds which will eventually lead to sulfate and nitrate containing aerosols/10/.

SO_2 also reacts with O_3, however the rate of oxidation is negligibly slow at ambient air temperature and at the low concentrations which are characteristic of O_3 and SO_2 in the troposphere. However, when alkanes are present in the O_3-SO_2 - air mixture, very fast SO_2 oxidation takes place, even in the dark. Under these conditions SO_2 is believed to be oxidized by the oxygenated radicals formed from reactions of alkenes with O_3, probably via Criegee intermediates, reactions 2-94 and 2-95.

$$O_2 + RCH{=}{=}CHR \rightarrow RCH\overset{O\text{-}O\text{-}O}{\diagup\!\!\diagdown}CHR \rightarrow RCHO + R\dot{C}HOO\cdot \qquad (2\text{-}94)$$

$$R\dot{C}HOO\cdot + SO_2 \rightarrow RCHO + SO_3 \qquad (2\text{-}95)$$

The rate of SO_2 oxidation is estimated to be approximately 0.23%, at 50% relative humidity (298°K), when the reactivity of the alkene towards O_3 is typical of that for an alkene with a terminal double bond/10/. The rate of this reaction is much lower than those rates expected for $\cdot OH$, $HO_2\cdot$ and $CH_3O_2\cdot$.

SO_3, formed as the product of many of the previously described SO_2 oxidations, reacts rapidly with singlet oxygen, $O(^3P)$, to give SO_4, equation 2-96, which decomposes to SO_2 and O_2, reaction 2-97.

$$SO_3 + O(^3P) + M \rightarrow SO_4 + M \quad (2\text{-}96)$$

$$\downarrow$$

$$SO_2 + O_2 + M \quad (2\text{-}97)$$

When $[SO_3]/[SO_2]$ is at steady state, SO_3 molecule encounters with $O(^3P)$ atoms will be much less frequent than those with the H_2O molecule which is abundant in the lower troposphere. Reaction of SO_3 with H_2O yields H_2SO_4, reaction 2-98.

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (2\text{-}98)$$

Removal of SO_3 by its reaction with H_2O is so very fast that reaction of SO_3 with any other species in the moist lower troposphere should be unimportant/10/.

2.5 Plume Chemistry

The previous sections presented a review of the chemistry of the major components of a well mixed polluted atmosphere. It can be concluded that the following species play important roles in photochemical smog formation: NO_2, NO, O_3, $\cdot OH$, SO_2, CO and hydrocarbons. The concentrations of each of these compounds are strongly interrelated. The major chemical species emitted by fossil fuel fired power plants include NO_x, CO and SO_2. The composition of the initial effluent from a power plant plume is therefore considerably different from that of a well mixed polluted atmosphere. The original effluent is oxygen depleted and rich in NO and SO_2. During the first stages of plume transport the very high NO levels and the very low hydrocarbon and CO concentrations result in the suppression of the long oxidation chains which ultimately lead to the relatively rapid conversion of SO_2 to SO_3, H_2SO_4, etc. NO_2 represents a small fraction of the plume gases released to the atmosphere. Additional NO_2 is formed as the ambient air (O_2) mixes in with the NO-rich gases during the early stages of plume dilution:

$$2\ NO + O_2 \rightarrow 2NO_2 \quad (2\text{-}55)$$

Because the initial $[NO_2]/[NO]$ ratio is low, the $[O_3]$ generated via reactions 2-30 to 2-32 will be far below the values observed in relatively clean, ambient air.

$$O(^3P) + O_2 (+M) \rightarrow O_3 (+M) \quad (2\text{-}30)$$

$$NO_2 + h\nu (\lambda < 3979\ \text{Å}) \rightarrow NO + O(^3P) \quad (2\text{-}31)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (2\text{-}32)$$

After a short mixing period, the ozone concentration should reach a photostationary state and can be related to the $[NO_2]/[NO]$ ratio as follows:

$$[O_3] \approx [NO_2]k_{2\text{-}31}/[NO]k_{2\text{-}32}$$

The ozone level within the plume will not reach "clean air" background values until the $[NO_2]/[NO]$ ratio climbs to near 2. Only after the plume gases have mixed with sufficient quantities of hydrocarbons, aldehydes, CO, etc, present in ambient air can extensive NO to NO_2 conversion be effected and O_3 levels climb.

When the O_2 concentration within the plume is relatively low and the concentration of SO_2 is high, the fraction of oxygen atoms captured by SO_2 can be significant. SO_2 is able to successfully compete with NO, NO_2, as well as O_2 for the singlet O-atoms formed from NO_2 photolysis. To illustrate, if the stack gases are at the following initial concentrations: [NO] = 500, $[SO_2]$ = 500, $[NO_2]$ = 20, $[O_2] = 1 \times 10^5$ ppm, then for a midday sun, the instantaneous oxidation of SO_2 via reaction 2-84 would be expected to be about 1.4% h^{-1}/10,11/.

$$O(^3P) + SO_2 (+M) \rightarrow SO_3 (+M) \quad (2\text{-}84)$$

As the plume is diluted the SO_2 oxidation rate falls rapidly.

Figure 2.3 summarizes the reactions of primary importance in the polluted atmosphere and further underlines their interdependence. Figure 2.4 illustrates the changes in the composition of the plume as a function of distance downwind from the stack/7a,b/.

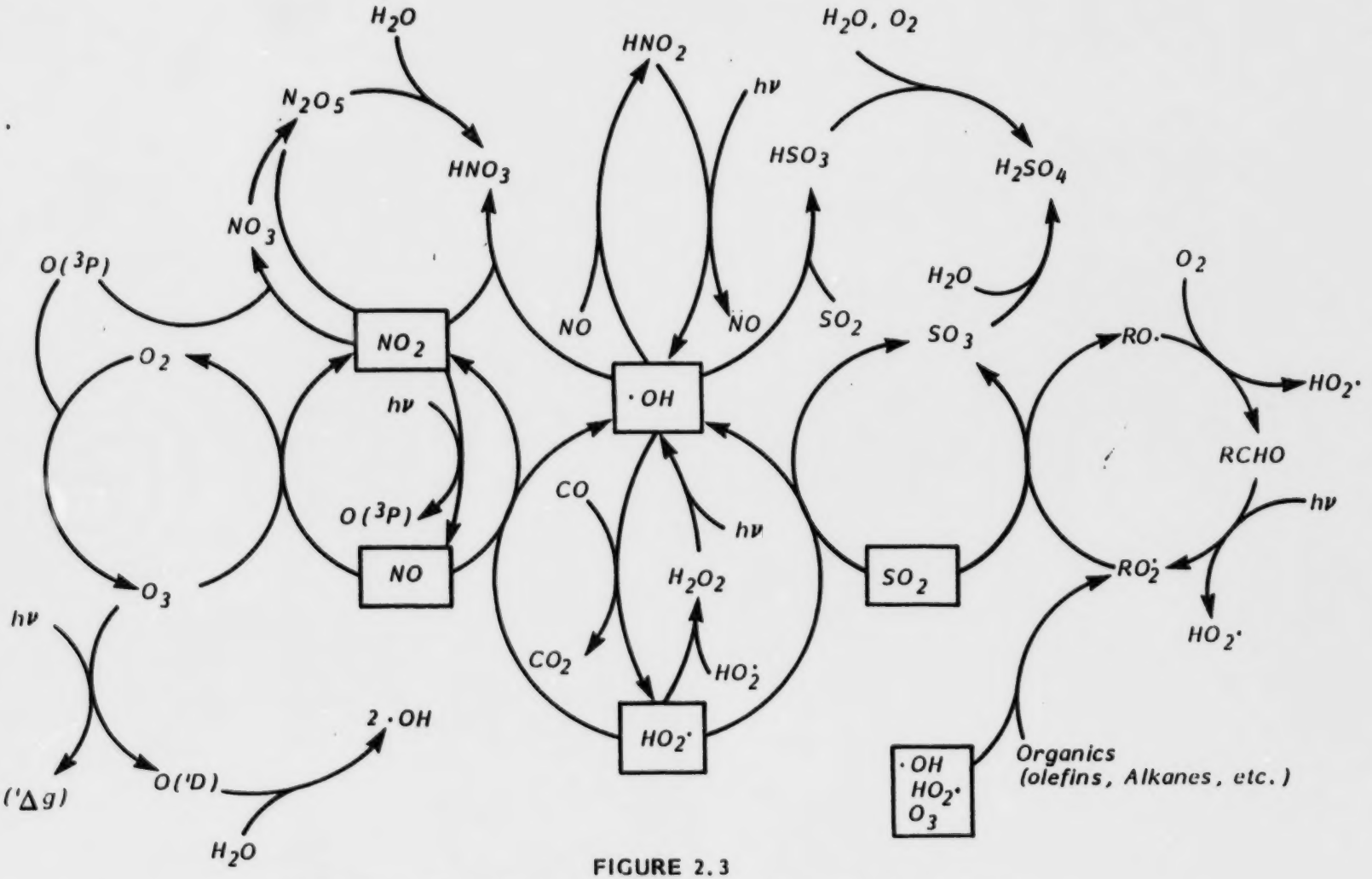


FIGURE 2.3

THE PRIMARY CHEMICAL SPECIES INVOLVED IN PHOTOCHEMICAL SMOG FORMATION AND THEIR REACTIONS

82-483

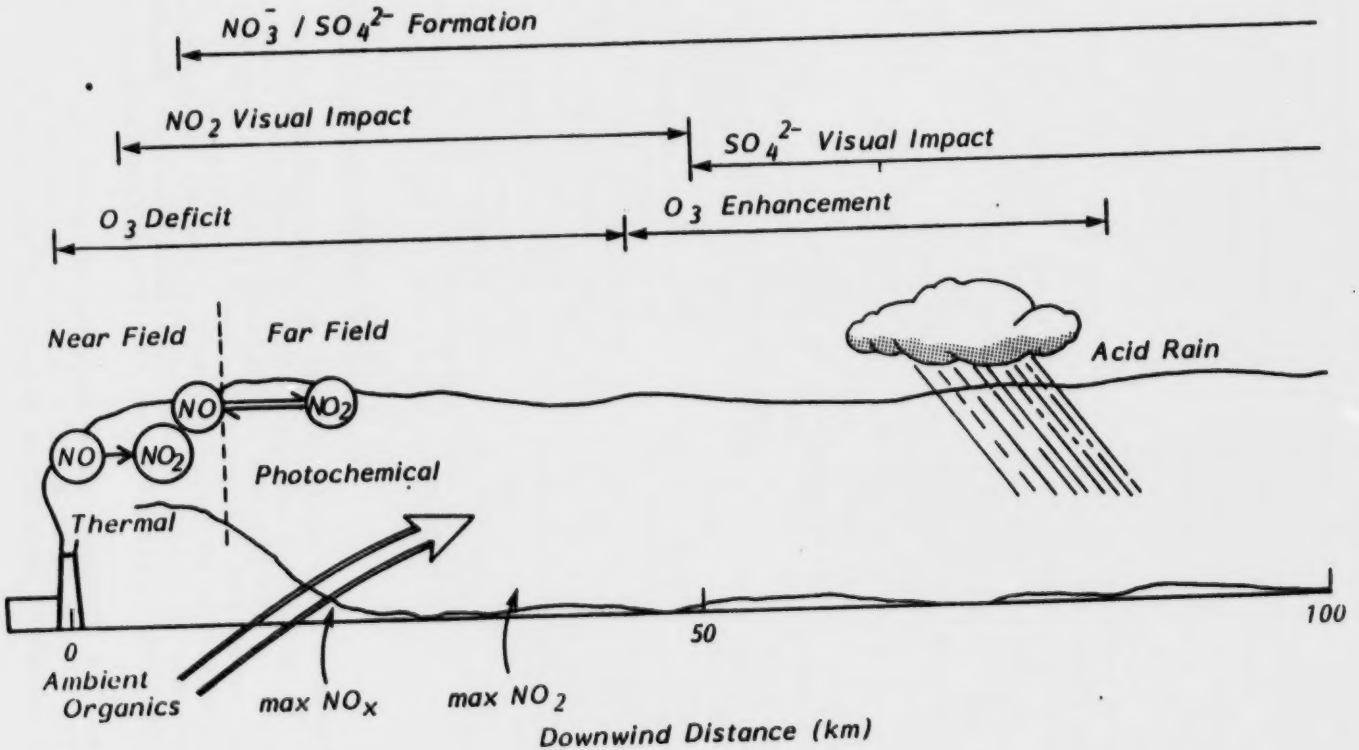


FIGURE 2.4

THE CHANGES IN THE COMPOSITION OF THE PLUME AS A FUNCTION OF DISTANCE DOWNWIND FROM THE STACKS. THE DISTANCES SHOWN ARE ONLY APPROXIMATE AND SHOULD NOT BE TAKEN AS ABSOLUTE. NOT ALL PROCESSES OCCUR UNDER ALL CONDITIONS (7)

3.0 PHOTOCHEMICAL MODELS

Section 2 presented a review of the primary chemical species and reactions involved in photochemical smog formation. The reactions can be written as first order differential equations in which the change in concentration of the reacting components, intermediates and products is expressed with respect to a change in time. Given the initial conditions and rate constants for the elementary reactions involved, the computer can be used to generate, by a numerical solution, reactant and product versus concentration time curves/15/. The large number of reactants and reactions involved in photochemical smog formation prohibits inclusion of all species and equations in a mathematical description of the mechanism. The high cost of computing time necessitates that the set of differential equations to be integrated be as compact as possible and consequently, only a limited degree of detail can be included in the kinetic mechanism. The number of equations required to describe smog formation can be reduced by grouping species with similar properties, ie, by lumping with respect to structure, reactivity and by eliminating those reactions with very slow rate constants. The set of reactions used to describe the mechanism of photochemical smog formation is referred to as a photochemical model. Many photochemical models or mathematical descriptions of smog formation have been reported. They differ in the number of reactions considered, the method by which the reactants are grouped and in the assignment of the rate constants for the lumped reactions. Photochemical models provide a unique technique for evaluating the impact of anthropogenic emissions on air quality. In this section, three of the most widely accepted photochemical models will be discussed, namely, (i) the Hecht-Seinfeld-Dodge Model, (ii) SCHEME/ATMOS and (iii) the Carbon Bond Mechanism. In addition, a mechanism recently reported by Atkinson et al will be examined. Although many other models have been published, they appear to be simple combinations and/or variations of the basic elements incorporated into the first three mechanisms.

3.1 Hecht-Seinfeld-Dodge Model 1974

The fundamental principle of the Hecht-Seinfeld-Dodge (H-S-D) mechanism/16/, reported in 1974, is the grouping of the large number of hydrocarbons involved in photochemical smog formation by class, ie, paraffin, olefin, aromatic and aldehyde. When this method of lumping is used, the products of the reactions of the various class hydrocarbons with O, O_3 and $\cdot OH$ are essentially the same within each group and can be accurately defined.

Hydrocarbons can also be grouped with respect to reactivity with compounds such as O, O_3 or $\cdot OH$. This method of lumping was not selected initially for the H-S-D mechanism because the rate

constants for reaction of hydrocarbons with O and O_3 do not necessarily correlate with groupings based on the ·OH rate. In addition, each group would contain hydrocarbons of all classes necessitating the use of stoichiometric coefficients to define the distribution of the products derived from each lumped group. To illustrate, if the hydrocarbons are divided into N groups on the basis of ·OH reactivity, the reactions with O, O_3 and ·OH can be written:

$$HC_i + O \overset{k_i}{\rightarrow} \alpha_{i1}R\cdot + \alpha_{i2}R\dot{C}O + \alpha_{i3}\dot{O}H$$

$$O_3 \overset{k_i'}{\rightarrow} \beta_{i1}R\dot{C}O + \beta_{i2}RO\cdot + \alpha_{i1}HC_1 + \ldots + \alpha_{iN}HC_N$$

$$\cdot OH \overset{k_i''}{\rightarrow} \partial_{i1}R + \partial_{i2}R\dot{C}O,$$

where i = 1, 2, ..., N and α_{ij}, β_{ij} and ∂_{ij} are stoichiometric coefficients which reflect the composition of HC_i. (If HC_i consists entirely of olefins, one might expect $\alpha_{i1} = \alpha_{i2} = 1$, $\alpha_{i3} = 0$.) The values of the parameters are fixed because of the choice of hydrocarbons comprising each lumped species, HC_i.

Lumping by hydrocarbon class rather than by reactivity was chosen by Hecht, Seinfeld and Dodge for two main reasons:

(i) fewer stoichiometric coefficients must be specified in the equations describing the reactions; and

(ii) rate constant values for hydrocarbon - ·OH reactions, at the time of publication, were not known precisely enough to permit a clear distinction to be made among hydrocarbons as to reactivity class.

The reactions describing the Hecht-Seinfeld-Dodge mechanism are listed in Table 3.1/16/. Olefins are represented by HC_1, aromatics by HC_2, paraffins by HC_3 and aldehydes by HC_4. Reactions 3-1 to 3-21 describe inorganic atmospheric chemistry and reactions 3-22 to 3-39 the atmospheric chemistry involving hydrocarbons. The only radical species considered in the H-S-D mechanism are ROO·, RCOO·, RO·, HO_2· and ·OH. This selection is

based on the following assumptions:

(i) alkyl radicals, R·, react very quickly with O_2 to form peroxyalkyl radicals, ROO·, therefore R· is not considered separately;

(ii) acyl radicals, RCO·, rapidly add O_2 to give peroxyacyl radicals, RCOO·, therefore only RCOO· is considered in the mechanism;

(iii) acylate radicals, RCO·, are omitted because they rapidly decompose to alkyl radicals, which quickly form peroxyalkyl radicals, and CO_2;

(iv) alkoxy radicals, RO·, are retained in the mechanism because they react with NO and NO_2 to give stable products.

The most important member of this group of radicals is ·OH and it is considered separately.

The reaction of ·OH with olefins, HC_1, is defined by reaction 3-24.

$$HC_1 + \cdot OH \rightarrow ROO\cdot + HC_4 \qquad (3\text{-}24)$$

·OH adds to the double bond of olefins to yield an alcohol-like free radical, $RCHCH_2\cdot$. This radical is assumed to react in the same fashion as an alkyl radical, R·, ie, to quickly add O_2 to form a peroxyalkyl radical, ROO·. However in subsequent reactions $RCHCH_2\cdot$, unlike R·, is thought to form one additional aldehyde. To account for this difference, an aldehyde (HC_4) is added to the reaction products.

Stoichiometric coefficients, α and β, are used in reactions 3-22, 3-29 and 3-30 (Table 3.1) to define the distribution of the products obtained from the different hydrocarbon classes, HC_i. α represents the fraction of carbons attached to the double bond in a monolefin which are not terminal carbons on the chain and β represents the fraction of total aldehydes which are not formaldehyde.

The reaction of aldehydes with ·OH is described in equation 3-30.

TABLE 3.1

THE HECHT-SEINFELD-DODGE MODEL (1974)/16/

Reaction		Rate Constant (k)[a]
$NO_2 + h\nu \rightarrow NO + 0$	(3-1)	0.266 min^{-1}
$O + O_2 + M \rightarrow O_3 + M$	(3-2)	2.0×10^{-5} ppm^{-2} min^{-1}
$O_3 + NO \rightarrow NO_2 + O_2$	(3-3)	20.8
$O + NO + M \rightarrow NO_2 + M$	(3-4)	3.5×10^{-3} ppm^{-2} min^{-1}
$O + NO_2 \rightarrow NO + O_2$	(3-5)	1.38×10^{4}
$O + NO_2 + M \rightarrow NO_3 + M$	(3-6)	2.2×10^{-3} ppm^{-2} min^{-1}
$O_3 + NO_2 \rightarrow NO_3 + O_2$	(3-7)	4.6×10^{-2}
$NO_3 + NO \rightarrow 2\ NO_2$	(3-8)	1.5×10^{4}
$NO_3 + NO_2 \rightarrow N_2O_5$	(3-9)	4.5×10^{3}
$N_2O_5 \rightarrow NO_2 + NO_3$	(3-10)	1.5×10^{1} min^{-1}
$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	(3-11)	1.0×10^{-5}
$NO + HNO_3 \rightarrow HNO_2 + NO_2$	(3-12)	2.5×10^{-4}
$HNO_2 + HNO_3 \rightarrow H_2O + 2\ NO_2$	(3-13)	0.2
$NO + NO_2 + H_2O \rightarrow 2\ HNO_2$	(3-14)	2.1×10^{-6} ppm^{-2} min^{-1}
$2\ HNO_2 \rightarrow NO + NO_2 + H_2O$	(3-15)	4.5
$HNO_2 + h\nu \rightarrow \cdot OH + NO$	(3-16)	1.3×10^{-2} min^{-1}
$\cdot OH + NO_2 \rightarrow HNO_3$	(3-17)	1.5×10^{4}
$\cdot OH + NO + M \rightarrow HNO_2 + M$	(3-18)	1.2×10^{4}[b]
$\cdot OH + CO + (O_2) \rightarrow CO_2 + HO_2\cdot$	(3-19)	2.5×10^{2}
$HO_2\cdot + NO \rightarrow \cdot OH + NO_2$	(3-20)	7.0×10^{2}
$H_2O_2 + h\nu \rightarrow 2\cdot OH$	(3-21)	$1/250\ k_{3-1}$ min^{-1}

Organic Oxidation Reactions:

HC_1 = olefins, HC_2 = aromatics, HC_3 = paraffins, HC_4 = aldehydes

$HC_1 + O \rightarrow ROO\cdot + \alpha RCOO\cdot + (1-\alpha)HO_2\cdot$ (3-22)		6.8×10^3
$HC_1 + O_3 \rightarrow RCOO\cdot + RO\cdot + HC_4$	(3-23)	1.6×10^{-2}
$HC_1 + \cdot OH \rightarrow ROO\cdot + HC_4$	(3-24)	2.5×10^4
$HC_2 + O \rightarrow ROO\cdot + \cdot OH$	(3-25)	1.07×10^2 C
$HC_2 + \cdot OH \rightarrow ROO\cdot + H_2O$	(3-26)	8×10^3 C
$HC_3 + O \rightarrow ROO\cdot + \cdot OH$	(3-27)	6.5×10^1
$HC_3 + \cdot OH \rightarrow ROO\cdot + H_2O$	(3-28)	3.8×10^3
$HC_4 + h\nu \rightarrow \beta ROO\cdot + (2-\beta)\ HO_2\cdot$	(3-29)	2.5×10^{-3} min^{-1}
$HC_4 + \cdot OH \rightarrow \beta RCOO\cdot + (1-\beta)\ HO_2\cdot + H_2O$	(3-30)	2.3×10^4
$ROO\cdot + NO \rightarrow RO\cdot + NO_2$	(3-31)	9.1×10^2
$RCOO\cdot + NO + (O_2) \rightarrow ROO\cdot + NO_2 + CO_2$	(3-32)	9.1×10^2
$RCOO\cdot + NO_2 \rightarrow RCOONO_2$	(3-33)	1.0×10^2
$RO\cdot + O_2 \rightarrow HO_2\cdot + HC_4$	(3-34)	2.4×10^{-2}
$RO\cdot + NO_2 \rightarrow RONO_2$	(3-35)	4.9×10^2
$RO\cdot + NO \rightarrow RONO$	(3-36)	2.5×10^2
$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$	(3-37)	5.3×10^3
$HO_2\cdot + ROO\cdot \rightarrow RO\cdot + \cdot OH + O_2$	(3-38)	1.0×10^2
$2ROO\cdot \rightarrow 2RO\cdot + O_2$	(3-39)	1.0×10^2

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a Units of ppm^{-1} min^{-1} unless otherwise indicated.
b Pseudosecond-order value.
c These values are for toluene.

$$HC_4 + \cdot OH \rightarrow \beta\ R\overset{O}{\overset{\|}{C}}OO\cdot + (1-\beta)\ HO_2\cdot + H_2O \qquad (3\text{-}30)$$

When HC_4 is HCHO, $\beta = 0$, the initial product is HCO· which decomposes to H· +CO. H· then reacts with O_2 to give HO_2· rather than the peroxyacyl radical. Reaction 3-30 therefore simplifies to 3-30a.

$$HC_4 + \cdot OH \rightarrow HO_2\cdot + H_2O \qquad (3\text{-}30a)$$

Problems arise when an attempt is made to use the mechanism to describe the behaviour of a complex mixture of hydrocarbons. If each hydrocarbon in class HC_i has a different value of α and a different rate constant for reaction with O, ·OH or O_3, then average rate constants must be calculated to describe the reactivity of each lumped group. However, average rate constants, chosen on the basis of the initial composition of the lumped group often do not accurately reflect the reactivity of the group at later times. A method is required with which the change in the average rate constant can be accounted for as the more reactive constituents of HC_i are consumed first. To overcome this difficulty, Hecht, Seinfeld and Dodge proposed a sublumping system based on the reactivity of members of each class with ·OH. A series of subgroups, HC_{ij}, is thereby generated. Within each subclass all species should react at comparable rates and the rate constants corresponding to HC_{ij} should not change with time. Thus, although the fundamental principle of the Hecht-Seinfeld-Dodge mechanism was the lumping of hydrocarbons on the basis of class, ie, paraffin, olefin, aromatic or aldehyde, in order for the mechanism to be of use in analyzing complex mixtures of hydrocarbons, each class must be subdivided according to reactivity with ·OH, or some other compound.

The Hecht-Seinfeld-Dodge mechanism was tested in a smog chamber using $HC/NO_x/O_3$ mixtures where the hydrocarbon (HC) was n-butane and/or propylene. The poor quality of the analytical techniques yielded concentrations which in many cases, when levels were below 0.15 ppm, could be determined no more accurately than $\pm$20%. No statistical measure of the reproducibility of the experiments was made. Difficulties were also encountered in calculating the light intensity and in estimating the effect of the chamber walls and water vapour. The results of the validation experiments were presented as concentration-time profiles for the various reactant mixtures, both predicted and

experimentally observed concentrations were plotted. The n-butane concentrations estimated by the mechanism matched the experimental data uniformly well over the full range of concentrations studied. The time to $[NO_2]$ maximum and the rate of NO oxidation agreed with the experimental data, however, the actual concentrations did not correlate. In general, the data and predictions were not always in good agreement for all species over the full period of the irradiation. The errors inherent in the analytical techniques, the generally poor correlation between the predicted and the observed concentrations (NO_2, NO, O_3) and the very simple pollutant mixtures modelled prevent definite statements about the utility of this kinetic mechanism in modelling the reactions of atmospheric pollutants.

3.2 Surrogate Chemical Mechanism (SCHEME)/ Atmospheric Model for Sulfur (ATMOS)

The Surrogate Chemical Mechanism (SCHEME)/17/ is a short, 12-species mechanism which models the homogeneous gas-phase reactions of pollutants in the atmosphere. It was derived from the Atmospheric Model for Sulfur (ATMOS)/18/, a 30-constituent reaction mechanism developed by Sander and Seinfeld in 1976 to model the chemistry of NO_x/hydrocarbon/SO_2 systems. The reactions describing the chemistry of the hydrocarbon/NO_x system were obtained from the Hecht-Seinfeld-Dodge model/16/. Some of the rate constant values were, however, revised and extra reactions were added. The reactions which describe the ATMOS mechanism are listed in Table 3.2/18/. ATMOS has been used to simulate the results of a 6 h irradiation of a typical urban pollution mixture containing 75 ppb NO, 25 ppb NO_2, 10 ppb SO_2, 100 ppb olefin and 10^4 ppb CO (initial concentrations). The results of these experiments suggested that the hydrocarbon/NO_x mechanism (modified Hecht-Seinfeld-Dodge scheme) was capable of simulating observed concentration-time behaviour in smog chamber systems when the hydrocarbon was propylene or 1-butene. The SO_2 oxidation rates could not, however, be explained solely on the basis of those SO_2 reactions presented in Table 3.2.

Additional reactions which might help to better describe SO_2 oxidation, but which are not listed in Table 3.2 include:

$$SO_2 + RO_2\cdot \rightarrow SO_3 + RO\cdot \qquad (3\text{-}108)$$

$$\rightarrow SO_2RO_2 \qquad (3\text{-}109)$$

$$SO_2 + RO\cdot \rightarrow ROSO_2 \qquad (3\text{-}110)$$

$$SO_2 + RCO(O_2)\cdot \rightarrow RCO_2\cdot + SO_3 \qquad (3\text{-}111)$$

For a system containing 0.1 ppm SO_2, 0.15 ppm NO, 0.05 ppm NO_2, 0.10 ppm C_4H_8 (1-butene), 10 ppm CO and 50% relative humidity, a maximum SO_2 oxidation rate of 4.5% h^{-1} was predicted. The reactions of SO_2 with $\cdot OH$ and $HO_2\cdot$, equations 3-92 and 3-93, Table 3.2, were believed to account for at least 90% of the predicted rate. The balance was assigned to the reaction of SO_2 with $RO_2\cdot$, equation 3-108, with $RCO_3\cdot$, equation 3-111, and with $O(^3P)$, equation 3-91, Table 3.2. Reactions 3-108 to 3-111 were not included in the ATMOS mechanism because the associated rate constants, at the time of publication, were essentially unknown. The necessity of including reactions 3-93 and 3-108 to 3-111 in the reaction mechanism is however questionable, recall from the discussion of SO_2 chemistry presented in Section 2.4, reaction of SO_2 with $\cdot OH$ appears to be the dominant path for the oxidation of SO_2 in the atmosphere.

The Surrogate Chemical Mechanism (SCHEME)/17/ was developed using the information gained from analyzing the simulation results obtained with ATMOS. The mechanism incorporates 28 reactions and models the concentration profiles of four initial reactant species (NO, NO_2, SO_2, olefin), four intermediate species (O_3, HONO, H_2O_2, aldehyde) and four free radicals ($HO\cdot$, $HO_2\cdot$, $RO_2\cdot$, $ROCOO_2\cdot$). The reduction in the size of the mechanism was accomplished by removing less important chemical species and reactions, and by employing surrogate rate constants and reactions to maintain the chemical integrity of the system. SCHEME accurately reproduces the results of ATMOS and reduces execution time by >80%. It is, however, only able to model photochemical smog formation as well as ATMOS.

3.3 Carbon Bond Mechanism

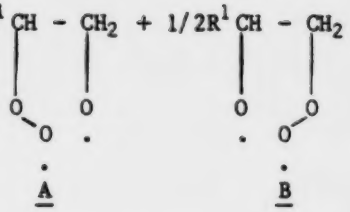
The Carbon Bond Mechanism (CBM)/19/ presents a unique approach to the modelling of the reactions of atmospheric pollutants. In this system, the carbon bond, rather than the molecule, is treated as the principal unit of reaction. The mechanism is based on the concept of analogously bonded carbon atoms reacting similarly and independently of the molecules in which they occur. For example, the single bonded carbon atoms in butane, 1-butene and butyraldehyde are treated as members of a single species, denoted as PAR (for paraffinic carbon atom). Since its introduction in 1980, the Carbon Bond Mechanism has undergone two major revisions resulting in the generation of CBM-II (1980)/20/ and CBM-III (1981)/19/. The changes were associated primarily with the classification of carbon-carbon double bonds. In the present version/19/, ethylene is considered as an explicit species, internal olefins are treated as carbonyls and a new aromatic chemical reaction scheme has been introduced. As a result of these modifications, the Carbon Bond Mechanism in its present form, CBM-III, includes the reactions of six types of carbon atoms:

TABLE 3.2

THE ATMOSPHERIC MODEL FOR SULFUR (ATMOS)/18/

Reaction		Rate Constant (25°C) (ppm^{-1} min^{-1})		
			Propylene $R^1 = CH_3$	1-Butene $R^1 = C_2H_5$
$NO_2 + h\nu \rightarrow NO + O$	(3-40)	$\phi I_a(1)$[a]		
$O + O_2 + M \rightarrow O_3 + M$	(3-41)	2×10^{-5}		
$NO + O_3 \rightarrow NO_2 + O_2$	(3-42)	29.5		
$O + NO + M \rightarrow NO_2 + M$	(3-43)	2.3×10^{-3}		
$O + NO_2 \rightarrow NO + O_2$	(3-44)	1.38×10^{4}		
$O + NO_2 + M \rightarrow NO_3 + M$	(3-45)	4.5×10^{-3}		
$NO_2 + NO_3 \rightarrow N_2O_5$	(3-46)	4.4×10^{3}		
$N_2O_5 \rightarrow NO_2 + NO_3$	(3-47)	13.8		
$NO + NO_3 \rightarrow 2\ NO_2$	(3-48)	1.48×10^{4}		
$O_3 + NO_2 \rightarrow NO_3 + O_2$	(3-49)	0.047		
$2NO + O_2 \rightarrow 2NO_2$	(3-50)	7.6×10^{-10}		
$O_3 + h\nu \rightarrow O + O_2$	(3-51)	ϕIa (0.035)[a]		
$O_3 + h\nu \rightarrow O(1_D) + O_2\ (^1\Delta)$	(3-52)	ϕIa (0.026)[a]		
$O(^1D) + M \rightarrow O + M$	(3-53)	1.1×10^{5}		
$O_2\ (^1\Delta_g) + O_3 \rightarrow 2O_2 + O$	(3-54)	5.6		
$\cdot OH + R^1CH = CH_2 \rightarrow R^1CH_2CH_2O\cdot$	(3-55)		390	1000
$\cdot OH + R^1CH = CH_2 \rightarrow R^1\dot{C}HOCH_3$	(3-56)		9400	2.3×10^{4}
$\cdot OH + R^1CH = CH_2 \rightarrow RO_2\cdot + H_2O$	(3-57)		1.5×10^{4}	3.6×10^{4}
$R^1CH_2CH_2O\cdot \rightarrow RO_2\cdot + ALD$	(3-58)		8500	8500
$R^1CH_2CH_2O\cdot + O_2 \rightarrow HO_2\cdot + ALD$	(3-59)		0.04	0.04
$R^1\dot{C}HOCH_3 \rightarrow RO_2\cdot + ALD$	(3-60)		8500	8500
$R_1\dot{C}HOCH_3 \rightarrow HO_2\cdot + R_1CCH_3$ (O)	(3-61)		0.04	0.04

$O_3 + R^1CH = CH_2 \rightarrow 1/2R^1CH - CH_2 + 1/2R^1CH - CH_2$



A B

	(3-62)		0.015	0.015
A + •OH + CO + HO_2• + ALD	(3-63)		1.7×10^4	4.5×10^5
B + •OH + ALD + RCO_3	(3-64)		1.7×10^4	4.5×10^5
A + ALD + Stable Products	(3-65)		1200	1.0×10^5
A + ALD + 1/2RO• + 1/2•OH + 1/2RCO_3• + 1/2CO +1/2HO_2•	(3-66)		1000	1000
B + ALD + CO + H_2O	(3-67)		1000	1000
O + $R^1CH = CH_2$ + RO_2• + 1/2RCO_3• + 1/2HO_2• + 1/2CO	(3-68)		5320	5900
NO + RO_2• → NO_2 + RO•	(3-69)	1000		
RO• + O_2 → HO_2• + ALD	(3-70)	0.024		
RO• + NO_2 → RNO_3	(3-71)	490		
RCO_3• + NO_2 → PAN	(3-72)	490		
•OH + NO → HNO_2	(3-73)	3000		
RO• + NO → RNO_2	(3-74)	2000		
NO + HO_2• → NO_2 + •OH	(3-75)	300		
NO_2 + •OH → HNO_3	(3-76)	1.2×10^4		
NO + RCO_3• → NO_2 + RO_2• + CO_2	(3-77)	910		
2RCO_3• → 2RO_2• + 2CO_2 + O_2	(3-78)	3.8		
2HO_2• → H_2O_2 + O_2	(3-79)	8200		
RO_2• + HO_2• → RO• + •OH + O_2	(3-80)	100		
ALD + hν → CO + HO_2• + 1/2RO_2•	(3-81)	$\emptyset I_a(0.01)^a$		
•OH + ALD → H_2O + 1/3CO + 1/3HO_2• + 2/3RCO_3•	(3-82)	2.2×10^4		
O_3 + •OH → HO_2• + O_2	(3-83)	87		
O^3 + HO^2• → •OH + $2O_2$	(3-84)	2		

$H_2O_2 + h\nu \rightarrow 2 \cdot OH$	(3-85)	$\phi I_a(0.0036)^a$
$HNO_2 + h\nu \rightarrow \cdot OH + NO$	(3-86)	$\phi I_a(0.07)^a$
$2HNO_2 \rightarrow NO + NO_2 + H_2O$	(3-87)	5.1×10^{-5}
$O(^1D) + H_2O \rightarrow 2 \cdot OH$	(3-88)	5.2×10^{5}
$NO + NO_2 + H_2O \rightarrow 2HNO_2$	(3-89)	2×10^{-6}
$\cdot OH + CO \rightarrow HO_2 \cdot + CO_2$	(3-90)	219
$O + SO_2 + M \rightarrow SO_3 + M$	(3-91)	2.8×10^{-5}
$\cdot OH + SO_2 \rightarrow HSO_3$	(3-92)	780
$HO_2 \cdot + SO_2 \rightarrow SO_3 + \cdot OH$	(3-93)	1.3
$NO_3 + SO_2 \rightarrow SO_3 + NO_2$	(3-94)	10^{-5}
$SO_3 + H_2O \rightarrow H_2SO_4$	(3-95)	1300
$O + SO_3 \rightarrow SO_2 + O_2$	(3-96)	0.082
$N_2O_5 + SO_2 \rightarrow SO_3 + 2NO_2$	(3-97)	6.2×10^{-7}
$O_3 + SO_2 \rightarrow SO_3 + O_2$	(3-98)	1.2×10^{-8}
$SO_2 + h\nu \rightarrow {}^1SO_2$	(3-99)	$\phi I_a(0.02)^a$
${}^1SO_2 + SO_2 \rightarrow SO_3 + SO$	(3-100)	5400
${}^1SO_2 + SO_2 \rightarrow {}^3SO_2 + SO_2$	(3-101)	4400
${}^1SO_2 + SO_2 + h\nu_f$	(3-102)	1.3×10^{6}
${}^1SO_2 \rightarrow {}^3SO_2$	(3-103)	9×10^{4}
${}^3SO_2 + SO_2 \rightarrow SO_3 + SO$	(3-104)	100
${}^3SO_2 \rightarrow SO_2 + h\nu_p$	(3-105)	8400
${}^3SO_2 \rightarrow SO_2$	(3-106)	7800
${}^3SO_2 + M \rightarrow SO_2 + M$	(3-107)	200

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a The quantity in parentheses is the value of the absolute photolysis rate constant relative to that for NO_2, $k_{(3-40)}$, for a solar spectral distribution and zenith angle of 40°.

(i) single-bonded carbon atoms, PAR (paraffinic molecules or single-bonded carbon atoms attached to other types of molecules);

(ii) relatively reactive double-bonded carbon atoms, OLE (olefins);

(iii) slow double bonds which are almost exclusively ethylene, ETH;

(iv) reactive aromatic rings, ARO;

(v) carbonyl compounds such as aldehydes and ketones, CARB; and

(vi) highly photolytic α-dicarbonyl compounds such as methyl glyoxal and biacetyl, DCRB.

The carbon number of each classification is fixed: PAR = 1; ETH = 2; OLE = 2 (double bonds are treated as pairs of carbons); ARO = 6 (an aromatic ring is considered to be three slow carbon-carbon double bonds); CARB = 1 (plus 1 oxygen atom); DCRB = 2 (plus 2 oxygen atoms). To illustrate the concept of carbon number, propylene, $CH_3CH = CH_2$, consists of one paraffinic bond and one double bond, 1 ppm of propylene would therefore yield 1 ppm of paraffinic bonds and 1 ppm of double bonds. The total number of reactive hydrocarbons (RHC) is calculated by summing the product of the concentration of each type of carbon fragment multiplied by its carbon number, equation 3-112.

$$([OLE] \times 2) + ([ETH] \times 2) + ([ARO] \times 6) + [CARB] + ([DCRB] \times 2) + [PAR] = RHC \text{ (in ppm C)} \quad (3\text{-}112)$$

In the case of propylene, RHC = ([OLE] x 2) + ([PAR] x 1) = 3 ppmC.

There are two exceptions to the rule of similar carbon-carbon bonds reacting identically, (i) internal olefins react much more rapidly than do terminal olefins, internal olefins are therefore treated as if they were already transformed to two carbonyls, and (ii) cycloparaffins are believed to be more reactive than linear paraffinic hydrocarbons and one CARB group is added to account for the extra reactive site formed when the ring splits.

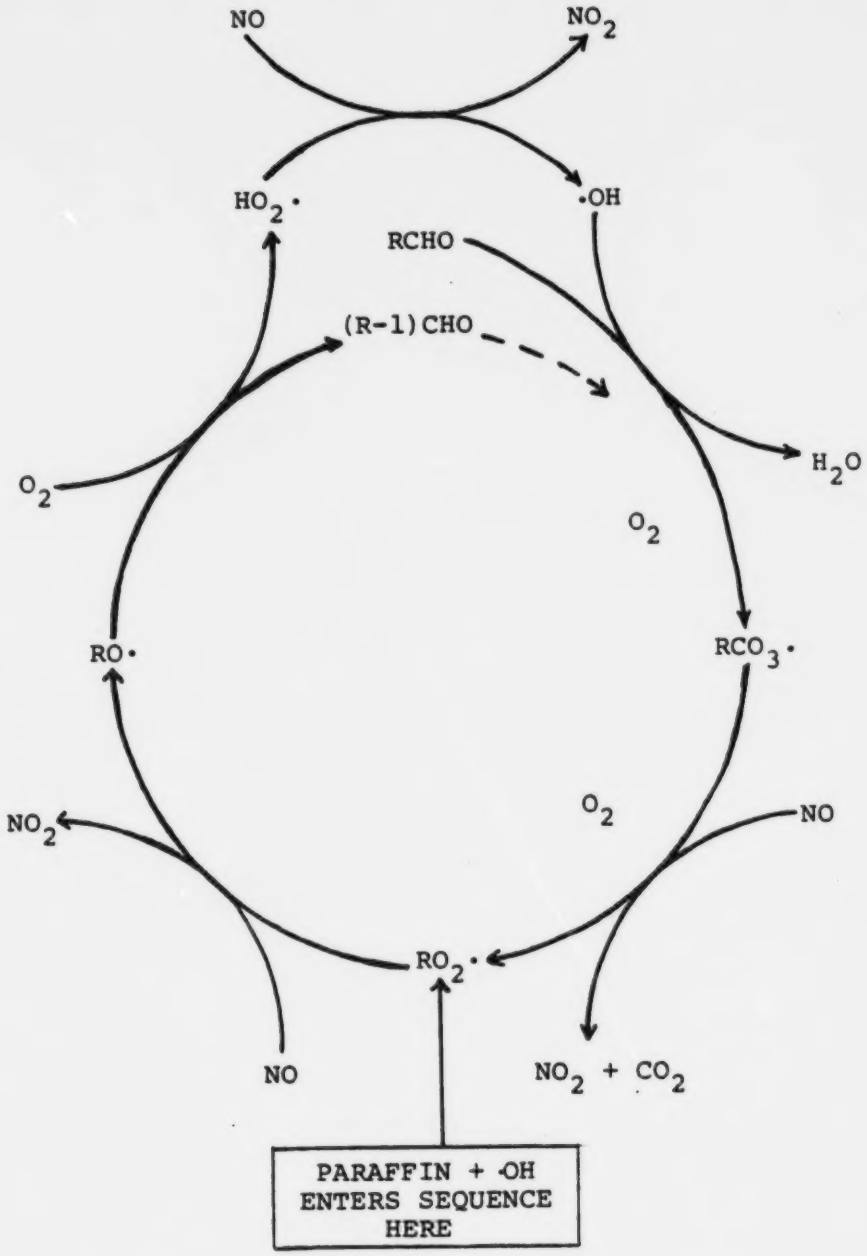
An important feature of looking at hydrocarbons in this way, relative to the approach used in molecular mechanisms, is that it offers a simple method for dealing with the chemistry of complex molecules, eg, cinnamaldehyde, $[(C_6H_5)CH = CHCHO]$. In the Carbon Bond Mechanism, cinnamaldehyde is treated as the sum of one ARO

group, one OLE group and one CARB unit (the carbon-carbon double bond may also be treated as one ETH unit or two CARB groups depending upon its reactivity). In contrast to this method of grouping, in mechanisms based on the molecular concept, cinnamaldehyde would be classified as either an aromatic, an olefin or an aldehyde. No matter into which class the molecule was lumped, the chemistry of the other two units would be ignored.

The Carbon Bond Mechanism has a number of advantages over the previously presented generalized mechanisms. In the Carbon Bond Mechanism no estimation of the molecular weight of the hydrocarbons in the various classes is required. The oxidation of hydrocarbons in smog is essentially a photochemically driven combustion process which culminates in the generation of CO_2 and H_2O. The stepwise disintegration of hydrocarbons is shown in Figure 3.1. Different hydrocarbons enter the process at select points in the cycle. The cycle is only a very basic representation of what takes place, but it does indicate that for each CH_2 group oxidized to CO_2, three molecules of NO are converted to NO_2.

Proper treatment of the stepwise oxidation of a mixture of hydrocarbons requires calculation of an average molecular weight. This is difficult in mechanisms in which the hydrocarbons are grouped by chemical type. During the oxidation cycle, the average molecular weight changes as the more reactive hydrocarbons are oxidized first. In the Hecht-Seinfeld-Dodge mechanism/16/, which is based on the grouping of hydrocarbons by chemical type, the reactions which describe the stepwise oxidation of the average carbon chain require the use of stoichiometric coefficients to reflect the change in composition of the group. However, the parameters vary with time and choosing a value for a complex hydrocarbon mixture as well as an average molecular weight remains a practical difficulty. In the Carbon Bond Mechanism, the carbon atoms are assumed to undergo reaction independently, so there is no stepwise oxidation of a hydrocarbon chain to consider and no data on average molecular weight is required. CBM allows the precise calculation of carbon mass balance in simulations, whereas such calculations can only be approximated when other mechanisms are used.

A second major advantage of the Carbon Bond Mechanism is that the range of rate constants to be averaged for the lumped hydrocarbon species can be reduced. To illustrate, the paraffins n-butane and isooctane react with $\cdot OH$ with rate constants of about 3800 and 11 500 $ppm^{-1}\ min^{-1}$. These reactivity rates normalized to the number of carbon atoms per molecule became 950 and 1440 $.ppmC^{-1}\ min^{-1}$, respectively. The range of rate constants to be averaged is thereby narrowed considerably.



Net Reaction: $RCHO + 3NO + 3O_2 \longrightarrow (R-1)CHO + 3NO_2 + CO_2 + H_2O$

Figure 3.1 A simplified description of the stepwise oxidation of hydrocarbons in smog /20/.

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The equations which define the Carbon Bond Mechanism, CBM-III, are presented in Table 3.3/19/. Table 3.4 lists the abbreviations used in Table 3.3. Many of the equations are the result of combining a number of reactions and chemical species. The derivation of these reactions and the chemistry they represent is discussed in the following.

The reactions describing carbon-carbon single bond chemistry are derived from the chemistry of alkanes (paraffins or RH). Alkanes undergo the following oxidation sequence (see also Figure 3.1):

$$RH + \cdot OH \xrightarrow{O_2} RO_2\cdot + H_2O \qquad (3\text{-}187)$$

$$RO_2\cdot + NO \xrightarrow{O_2} HO_2\cdot + RCHO + NO_2 \qquad (3\text{-}188)$$

$$HO_2\cdot + NO \rightarrow \cdot OH + NO_2 \qquad (3\text{-}125)$$

In this series of reactions, one hydroxyl radical reacts and is regenerated, two molecules of NO are converted to NO_2, and the alkane is converted to an aldehyde. These reactions are translated into the CBM-III "language" with the following changes: RH is replaced by PAR, where [PAR] = n[RH] + m[CX], n is the number of carbon atoms in all alkanes, RH, and m is the number of all other single-bonded carbon atoms attached to other types of molecules; $RO_2\cdot$ is replaced by MEO_2 and RCHO is replaced by CARB, equations 3-128 and 3-142 (Table 3.3), respectively.

Reaction 3-127 was introduced to preserve carbon mass balance.

$$PAR + X \rightarrow \qquad (3\text{-}127)$$

This type of "correction" reaction is required because of reactions such as 3-148 in which ACO_3, a two carbon species, is produced from the reaction of $\cdot OH$ with the single carbon carbonyl species, CARB.

$$\cdot OH + CARB \xrightarrow{O_2} ACO_3 + X \qquad (3\text{-}148)$$

The method of correction arises from the reaction of $RCO_3\cdot$ ($R>CH_3$) with NO to produce NO_2, CO_2 and $RO_2\cdot$. This reaction results in the oxidation of the carbon adjacent to the CO_3 group in $RCO_3\cdot$. In terms of the CBM, it results in the conversion of a PAR species (a single or paraffinic bond) to MEO_2 (a one carbon

TABLE 3.3

CARBON BOND MECHANISM-III

Reaction		Rate Constant at 298°K ($ppm^{-1}\ min^{-1}$)
$NO_2 \rightarrow NO + O$	(3-113)	a
$O + (O_2) + (M) \rightarrow O_3$	(3-114)	4.40×10^6 b
$NO + O_3 \rightarrow NO_2 + O_2$	(3-115)	26.6
$NO_2 + O_3 \rightarrow NO_3 + O_2$	(3-116)	0.048
$NO_2 + O \rightarrow NO + O_2$	(3-117)	1.3×10^4
$OH + O_3 \rightarrow HO_2 + O_2$	(3-118)	100
$HO_2 + O_3 \rightarrow OH + 2O_2$	(3-119)	2.40
$OH + NO_2 \rightarrow HNO_3$	(3-120)	1.60×10^4
$OH + CO \xrightarrow{O_2} HO_2 + CO_2$	(3-121)	440
$NO + NO + (O_2) \rightarrow NO_2 + NO_2$	(3-122)	1.50×10^{-4} b
$NO + NO_3 \rightarrow NO_2 + NO_2$	(3-123)	2.80×10^4
$NO_2 + NO_3 + H_2O \rightarrow 2HNO_3$	(3-124)	c
$NO + HO_2 \rightarrow NO_2 + OH$	(3-125)	1.20×10^4
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	(3-126)	1.50×10^4
$X + PAR \rightarrow$	(3-127)	10^5
$OH + PAR \xrightarrow{O_2} MEO_2 + H_2O$	(3-128)	1300
$O + OLE \xrightarrow{O_2} MEO_2 + ACO_3 + X$	(3-129)	2700
$O + OLE \rightarrow CARB + PAR$	(3-130)	2700
$OH + OLE \xrightarrow{O_2} RAO_2$	(3-131)	3.70×10^4
$O_3 + OLE \rightarrow CARB + CRIG$	(3-132)	0.008

$O_3 + OLE \xrightarrow{O_2} CARB + MCRG + X$	(3-133)	0.008
$O + ETH \xrightarrow{O_2} MEO_2 + HO_2 + CO$	(3-134)	600
$O + ETH \rightarrow CARB + PAR$	(3-135)	600
$OH + ETH \xrightarrow{O_2} RBO_2$	(3-136)	1.20×10^4
$O_3 + ETH \rightarrow CARB + CRIG$	(3-137)	0.0024
$NO + ACO_3 \xrightarrow{O_2} NO_2 + MEO_2$	(3-138)	1.04×10^4
$NO + RBO_2 \xrightarrow{O_2} NO_2 + CARB + HO_2 + CARB$	(3-139)	1.20×10^4
$NO + RAO_2 \xrightarrow{O_2} NO_2 + CARB + HO_2 + CARB$	(3-140)	1.20×10^4
$O + MEO_2 \xrightarrow{O_2} NO_2 + CARB + MEO_2 + X$	(3-141)	3800
$NO + MEO_2 \xrightarrow{O_2} NO_2 + CARB + HO_2$	(3-142)	7700
$NO + MEO_2 \rightarrow NRAT$	(3-143)	500
$O_3 + RBO_2 \rightarrow CARB + CARB + HO_2 + O_2$	(3-144)	5.0
$O_3 + RAO_2 \rightarrow CARB + CARB + HO_2 + O_2$	(3-145)	200
$OH + CARB \rightarrow CRO_2 + X$	(3-146)	1000
$OH + CARB \xrightarrow{O_2} HO_2 + CO$	(3-147)	7000
$OH + CARB \xrightarrow{O_2} ACO_3 + X$	(3-148)	6000
$CARB \rightarrow CO + H_2$	(3-149)	$(\approx 0.002\ K_{(3-113)})a$
$CARB + (O_2) \xrightarrow{O_2} 2/3\ (2HO_2 + CO)$ $1/3\ (2MEO_2 + CO + 2X)$	(3-150)	$(\approx 0.002\ K_{(3-113)})a$
$NO_2 + ACO_3 \rightarrow PAN$	(3-151)	7000
$PAN \rightarrow ACO_3 + NO_2$	(3-152)	0.022

$HO_2 + ACO_3 \rightarrow$ Stable Products	(3-153)	1.50×10^4
$HO_2 + MEO_2 \rightarrow$ Stable Products	(3-154)	9000
$NO + CRIG \rightarrow NO_2 + CARB$	(3-155)	1.20×10^4
$NO_2 + CRIG \rightarrow NO_3 + CARB$	(3-156)	8000
$CARB + CRIG \rightarrow$ Ozonide	(3-157)	2000
$NO + MCRG \rightarrow NO_2 + CARB + PAR$	(3-158)	1.20×10^4
$NO_2 + MCRG \rightarrow NO_3 + CARB + PAR$	(3-159)	8000
$CARB + MCRG \rightarrow$ Ozonide	(3-160)	2000
$CRIG \rightarrow CO + H_2O$	(3-161)	670^e
$CRIG \rightarrow$ Stable Products	(3-162)	240^e
$CRIG \xrightarrow{O_2} HO_2 + HO_2 + CO$	(3-163)	90^e
$MCRG \rightarrow$ Stable Products	(3-164)	150^e
$MCRG \xrightarrow{O_2} MEO_2 + OH + CO$	(3-165)	340^e
$MCRG \xrightarrow{O_2} MEO_2 + HO_2$	(3-166)	425^e
$MCRG \xrightarrow{O_2} CARB + HO_2 + CO + HO_2$	(3-167)	85^e
$OH + ARO \xrightarrow{O_2} RARO + H_2O$	(3-168)	6000
$OH + ARO \xrightarrow{O_2} HO_2 + OPEN$	(3-169)	1.45×10^4
$NO + RARO \xrightarrow{O_2} NO_2 + PHEN + HO_2$	(3-170)	4000
$OPEN + NO \xrightarrow{O_2} NO_2 + DCRB + X + APRC$	(3-171)	6000
$APRC \xrightarrow{O_2} DCRB + CARB + CO$	(3-172)	$10^4\,e$
$APRC \xrightarrow{O_2} CARB + CARB + CO + CO$	(3-173)	$10^4\,e$

$PHEN + NO_3 \rightarrow PHO + HNO_3$	(3-174)	5000
$PHO + NO_2 \rightarrow NPHN$	(3-175)	4000
$PHO + HO_2 \rightarrow PHEN + O_2$	(3-176)	5.00×10^4
$OPEN + O_3 \rightarrow DCRB + X + APRC$	(3-177)	40
$OH + PHEN \xrightarrow{O_2} HO_2 + APRC + PAR + CARB$	(3-178)	3.00×10^4
$DCRB \xrightarrow{O_2} 1/2\ (HO_2 + ACO_3 + CO) + 1/2\ (MEO_2 + HO_2 + 2CO)$	(3-179)	$(\approx 0.04\ K_{(3-113)})$[a]
$PHEN + OH \rightarrow PHO$	(3-180)	10^4
$CRO_2 + NO \xrightarrow{O_2} NO_2 + HO_2 + DCRB$	(3-181)	1.20×10^4
$HONO \rightarrow OH + NO$	(3-182)	$(\approx 0.06\ K_{(3-113)})$[a]
$OH + NO \rightarrow HONO$	(3-183)	9770
$O_3 \rightarrow O^1D$	(3-184)	$(\approx 10^{-3}\ K_{3-113})$[a]
$O^1D \xrightarrow{+(M)} O$	(3-185)	4.44×10^{10}
$O^1D + H_2O \rightarrow OH + OH$	(3-186)	3.4×10^5

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a Sunlight-dependent; units of min^{-1}.
b Units of $ppm^{-2}\ min^{-1}$.
c Heterogeneous; pseudo third order. Equal to $591 \times k(N_2O_5 + H_2O)$.
d The rate of nitrate formation varies according to the hydrocarbon composition. Killus and Whitten/19/ recommend the default value of 500 $ppm^{-1}\ min^{-1}$. This was found to be the best value for a hydrocarbon mixture whose paraffin content most closely resembles that of urban environments.
e Units of min^{-1}.

TABLE 3.4

ABBREVIATIONS USED IN TABLE 3.3

ACO_3	Peroxyacyl radical (two-carbon surrogate for RCO_3)
APRC	Aromatic product carbon
ARO	Aromatic ring
ARPI	Aromatic oxidation intermediate product
CARB	Carbonyl bond
CRIG	Criegee intermediate (H_2CO_2)
CRO_2	Carbonyl peroxy which will produce DCRB
DCRB	Dicarbonyl compound
ETH	Ethylene or slow olefinic bond
GLY	Surrogate for dicarbonyls
KET	Ketone
MCRG	Surrogate for $RCHO_2$ type Criegee intermediates
MEO_2	Peroxy radical (one-carbon surrogate for RO_2)
NPHN	Nitrophenol
NRAT	Organic nitrate
OLE	Olefinic bond
OPEN	Aromatic ring-opening intermediate
PAN	Peroxyacyl nitrate
PAR	Single or paraffinic bond
PHEN	Phenolic pathway surrogate in ARO oxidation
PHO	Phenoxy radical
RAO_2	Hydroxyperoxyl from $\cdot OH + OLE$
RARO	Aromatic radical

RBO_2	Hydroxyperoxyl from ·OH + ETH
RCO_3	Peroxyacyl radical
RO	Alkoxyl radical
RO_2	Peroxy radical
X	Carbon-mass balancing unit

surrogate for $RO_2\cdot$). Therefore whenever an extra carbon atom appears on the right side of a chemical reaction, one X is produced that immediately removes one PAR via reaction 3-127. Generally, X accounts for the oxidation of a single bonded carbon atom from the PAR pool by pathways other than direct reaction with ·OH. One such route is the oxidation of paraffins by singlet oxygen, a reaction which is otherwise not included in the CBM-III.

Equations 3-184 to 3-186 describe the reactions of $O(^1D)$, the photolysis product of O_3. The photolysis reaction of O_3 is believed to be most important in rural areas where the concentration of NO is lower and the level of O_3 is much higher than the corresponding concentrations detected in urban areas. It is suggested that in urban applications, $O(^1D)$ chemistry is relatively unimportant and can often be omitted.

Reaction of olefins with the hydroxyl radical, ·OH, leads to the formation of an initial addition product which in air is $HORO_2\cdot$, equation 3-131. $HORO_2\cdot$ reacts with O_3 to form two aldehydes, CARB, equation 3-145.

$$\cdot OH + OLE \xrightarrow{O_2} RAO_2 \qquad (3\text{-}131)$$

(RAO_2 = hydroxyl peroxyl, $HORO_2\cdot$)

$$O_3 + RAO_2 \rightarrow CARB + CARB + HO_2\cdot + O_2 \qquad (3\text{-}145)$$

The carbonyl products can undergo a number of oxidation reactions, including photolysis, equations 3-149 and 3-150; and oxidation by hydroxyl radicals, reactions 3-189 and 3-190.

$$CARB + h\nu \rightarrow H_2 + CO \qquad (3\text{-}149)$$

$$CARB + h\nu \xrightarrow{O_2} 2/3\ (2\ HO_2\cdot + CO) \qquad (3\text{-}150)$$

$$\xrightarrow{O_2} 1/3\ (2\ MEO_2 + CO + 2X)$$

$$RCHO + \cdot OH \rightarrow ACO_3 + H_2O \qquad (3\text{-}189)$$

$$\rightarrow HO_2\cdot + CO + H_2O \quad (R=H) \qquad (3\text{-}190)$$

In terms of the CBM-III notation, equations 3-189 and 3-190 translate to equations 3-147 and 3-148. Ketone oxidation is more complex and is shown in equations 3-191 to 3-193.

$$CH_3COCH_2CH_3 + \cdot OH \overset{O_2}{\rightarrow} CH_3COCH\dot{O}_2CH_3 \ (+ H_2O) \qquad (3\text{-}191)$$

$$CH_3COCH\dot{O}_2CH_3 + NO \rightarrow NO_2 + CH_3COCH\dot{O}CH_3 \qquad (3\text{-}192)$$

$$CH_3COCH\dot{O}CH_3 + O_2 \rightarrow HO_2\cdot + CH_3COCOCH_3 \qquad (3\text{-}193)$$

(biacetyl)

Using the language of CBM-III, reactions 3-191 to 3-193 translate to 3-146 and 3-181. (CARB is also used to represent ketones.)

$$CARB + \cdot OH \rightarrow CRO_2 + X \qquad (3\text{-}146)$$

(CRO_2 = carbonyl peroxy)

$$CRO_2 + NO \rightarrow NO_2 + HO_2\cdot + DCRB \qquad (3\text{-}181)$$

(DCRB = dicarbonyl species)

The reactions of alkyl peroxyl radicals include:

$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2 \qquad (3\text{-}194)$$

$$RO_2\cdot + NO \rightarrow \text{nitrates} \qquad (3\text{-}195)$$

$$RO\cdot + O_2 \rightarrow \text{aldehyde} + HO_2\cdot \qquad (3\text{-}196)$$

$$\rightarrow HORO_2\cdot \text{ (isomerization)} \qquad (3\text{-}197)$$

$$RO_2\cdot \overset{O_2}{\rightarrow} R'O_2\cdot + \text{aldehyde (decomposition)} \qquad (3\text{-}198)$$

$$RO_2\cdot + HO_2\cdot \rightarrow \text{stable products} \qquad (3\text{-}199)$$

Reactions 3-197 and 3-198 occur in systems with carbon chains greater than or equal to four. In the CBM-III reactions 3-194 and 3-196 are written as a single step, equation 3-142, and

$$MEO_2 + NO \rightarrow NO_2 + CARB + HO_2\cdot \qquad (3\text{-}142)$$

reactions 3-197 and 3-198 are condensed to reaction 3-141.

$$MEO_2 + NO \rightarrow NO_2 + CARB + (MEO_2 + X) \qquad (3\text{-}141)$$

Reaction 3-195 translates to equation 3-143 and 3-199 to equation 3-154.

$$MEO_2 + NO \rightarrow \text{nitrates (NRAT)} \qquad (3\text{-}143)$$

$$MEO_2 + HO_2\cdot \rightarrow \text{stable products} \qquad (3\text{-}154)$$

Aromatic oxidation is described in the CBM-III with the following reactions:

$$ARO + \cdot OH \xrightarrow{O_2} OPEN + HO_2\cdot \quad , \qquad (3\text{-}169)$$

where OPEN represents the intermediate of the ring opening reaction.

$$OPEN + NO \xrightarrow{O_2} NO_2 + DCRB + APRC + X \qquad (3\text{-}171)$$

$$OPEN + O_3 \rightarrow DCRB + APRC + X, \qquad (3\text{-}177)$$

where APRC represents the aromatic product left after the dicarbonyl species has been removed.

The product represented by APRC can react further to give glyoxal (GLY) or another dicarbonyl species:

$$APRC \xrightarrow{O_2} DCRB + GLY \qquad (3\text{-}200)$$

$$\rightarrow GLY + GLY \qquad (3\text{-}201)$$

Glyoxal, $(CHO)_2$, reacts with $\cdot OH$ to give HCO which decomposes to $HO_2\cdot$ and CO, reactions 3-202 and 3-203.

$$(CHO)_2 + \cdot OH \rightarrow H_2O + HCO + CO \qquad (3\text{-}202)$$

$$HCO \rightarrow HO_2\cdot + CO \qquad (3\text{-}203)$$

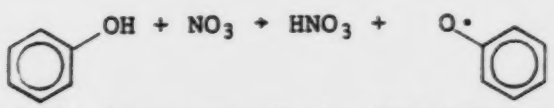
Reactions 3-202 and 3-203 can be combined to give equation 3-204, which when substituted into equations 3-200 and 3-201, yields reactions 3-172 and 3-173.

$$GLY \rightarrow CARB + CO \qquad (3\text{-}204)$$

$$APRC \xrightarrow{O_2} DCRB + CARB + CO \qquad (3\text{-}172)$$

$$APRC \xrightarrow{O_2} CARB + CARB + CO + CO \qquad (3\text{-}173)$$

Phenolic hydrocarbons may serve as both radical and NO_x sinks. NO_3 reacts with phenol as shown in equation 3-205.



(3-205)

In the language of the CBM-III, reaction 3-205 translates to 3-174.

$$PHEN + NO_3 \rightarrow PHO + HNO_3, \qquad (3\text{-}174)$$

where PHEN represents phenol, PHO represents the phenoxy radical.

Reaction of phenol with $\cdot OH$ also yields the phenoxy radical, equation 3-206.

$$PHEN + \cdot OH \rightarrow PHO \qquad (3\text{-}206)$$

PHO can react with NO_2 to yield nitrophenol, NPHN, equation 3-175, or with $HO_2\cdot$ to regenerate phenol, equation 3-176.

$$PHO + NO_2 \rightarrow NPHN \qquad (3\text{-}175)$$

$$PHO + HO_2\cdot \rightarrow PHEN + O_2 \qquad (3\text{-}176)$$

Reaction 3-176 is a potentially important radical sink in aromatic systems.

When the aromatic hydrocarbon is benzaldehyde (BZA), its oxidation reaction is lumped with ·OH addition to the aromatic ring, equation 3-168. The product, an aromatic radical, RARO, reacts with NO to give phenol as shown in equation 3-170.

$$ARO + \cdot OH \xrightarrow{O_2} RARO + H_2O \qquad (3\text{-}168)$$

$$RARO + NO \rightarrow NO_2 + HO_2\cdot + PHEN \qquad (3\text{-}170)$$

The ability of the CBM-III to simulate photochemical smog formation was tested in a smog chamber with eleven modelling experiments using three different hydrocarbon/NO_x mixtures/19/. The hydrocarbon fractions contained varying amounts of olefins, paraffins and aromatics. The experimental results were plotted as concentration versus time curves. For all three hydrocarbon mixtures a very good correlation between predicted and measured concentrations was found. The rate of nitrate formation, reaction 3-143, did however have to be changed according to the hydrocarbon mixture used. Overall, the validation results reported by Killus and Whitten/19/, suggest the Carbon Bond Mechanism to be very useful for modelling photochemical smog formation. Unfortunately, the mechanism was designed to model a hydrocarbon rich polluted atmosphere, eg, one which arises from automobile exhaust, and the contribution of SO_2 to smog formation was not considered.

3.4 Atkinson's Model

A photochemical model describing hydrocarbon/NO_x/SO_2 photooxidation has recently been reported by Atkinson et al/22/. In this mechanism the hydrocarbons are separated into the following groups: propane, alkanes containing >4 carbon atoms,

ethene, 1-alkenes, internal alkenes, benzene, monoalkylbenzenes, dialkylbenzenes, formaldehyde, acetaldehyde, higher aldehydes and ketones. These groupings are based predominantly on OH radical reaction rate constants. Methane and ethane were regarded as nonreactive and therefore neglected. The reactions which define the model are listed in Table 3.5.

As in the Carbon Bond Mechanism/19/, many of the reactions which describe the model are the result of combining two or more elementary reactions. This technique helps to minimize the number of reactants required to define the mechanism and thereby helps to conserve computer time and concomitant cost.

The reaction mechanism was tested in a smog chamber using single hydrocarbon-NO_x-air mixtures, multihydrocarbon-NO_x-air mixtures and four selected hydrocarbon-NO_x-SO_2-air mixtures. The results of these studies yielded good fits between the experimental and calculated concentration-time profiles/22/.

The mechanism, as listed in Table 3.5/22/, is very long but can be shortened by further amalgamation of reaction steps. To illustrate, all $RO_2\cdot + NO_2$ reactions, where R = hydrocarbon function, were eliminated via condensation of the following reaction steps:

$$RCO_3\cdot + NO \rightarrow C_2H_5O_2 + NO_2 \qquad (3\text{-}207)$$

$$C_2H_5O_2 + NO \xrightarrow{O_2} CH_3CHO + HO_2\cdot + NO_2 \qquad (3\text{-}208)$$

to yield:

$$RCO_3\cdot + NO \rightarrow CH_3CHO + 2NO_2 + HO_2\cdot - NO \qquad (3\text{-}209)$$

It was also found that neglecting propane, benzene and acetone and replacement of RCHO by CH_3CHO had little effect (<2%) on the NO, NO_2 and O_3 time-concentration profiles. As a result the species propane, benzene, acetone, RCHO, RCO_3 and PPN were omitted in the abbreviated version of the model.

3.5 Summary and Conclusions

This section presented four mechanisms which have been used to model photochemical smog formation: i) the Hecht-Seinfeld-Dodge Model (H-S-D), ii) ATMOS/SCHEME, iii) the Carbon Bond Mechanism and iv) the Atkinson mechanism. The greatest and most common weakness found in almost all photochemical models reported in

TABLE 3.5

ATKINSON'S MODEL/22/

Reaction Inorganics		Rate Constant[a]	
$NO_2 + h\nu \xrightarrow{O_2} NO + O_3$	(3-210)	variable	
$NO + O_3 \rightarrow NO_2 + O_2$	(3-211)	$1.0\times10^{6}T^{-1}e^{-1450/T}$	
$O_3 + h\nu \rightarrow 2 \cdot OH$	(3-212)	$\beta_1 k_{(3-210)} \times 7.5\times10^{-6}[H_2O]$	
$\cdot OH + NO \xrightarrow{M} HONO$	(3-213)	$8.7\times10^{8}T^{-2}$	(1)
$\cdot OH + NO_2 \xrightarrow{M} HNO_3$	(3-214)	$1.5\times10x^{9}T^{-2}$	(1)
$HONO + h\nu \rightarrow \cdot OH + NO$	(3-215)	$\beta_2 k_{(3-210)}$	
$HO_2\cdot + NO \rightarrow \cdot OH + NO_2$	(3-216)	$3.7\times10^{6}T^{-1}$	(1)
$HO_2\cdot + NO_2 \xrightarrow{M} HO_2NO_2$	(3-217)	$1.5\times10^{8}T^{-2}$	(1)
$HO_2NO_2 \xrightarrow{M} HO_2\cdot + NO_2$	(3-218)	$7.5\times10^{15}e^{-10420/T}$	(2)
$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$	(3-219)	$3.4\times10^{4}T^{-1}e^{1100/T} + 5.8\times10^{-5}T^{-2}e^{5800/T}[H_2O]$	
$H_2O_2 + h\nu \rightarrow 2 \cdot OH$	(3-220)	$\beta_3 k_{(3-210)}$	
$\cdot OH + CO \xrightarrow{O_2} HO_2\cdot$	(3-221)	$1.3\times10^{-5}T^{-1}$	
$NO_2 + O_3 \rightarrow NO_3$	(3-222)	$5.3\times10^{4}T^{-1}e^{-2450/T}$	
$NO + NO_3 \rightarrow 2\ NO_2$	(3-223)	$8.4\times10^{6}T^{-1}$	
$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(3-224)	$3.1\times10^{7}T^{-1}e^{-1100/T}$	
$N_2O_5 \xrightarrow{M} NO_2 + NO_3$	(2-225)	$3.5\times10^{18}e^{-12280/T}$	

$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	(3-226)	$\sim 1.33 \times 10^{-3} T^{-1}$	(3)
$NO_3 + h\nu \rightarrow 0.3NO + 0.7\ NO_2 + 0.7\ O_3$	(3-227)	$\beta_4 k_{(3-210)}$	
$\cdot OH + O_3 \rightarrow HO_2\cdot$	(3-228)	$7.0 \times 10^5 T^{-1} e^{-940/T}$	
$HO_2\cdot + O_3 \rightarrow \cdot OH$	(3-229)	$4.8 \times 10^3 T^{-1} e^{-580/T}$	

Formaldehyde

$HCHO + h\nu \xrightarrow{O_2} 2HO_2\cdot + CO$	(3-230)	$\beta_5 k_{(3-210)}$
$HCHO + h\nu \rightarrow CO + H_2$	(3-231)	$\beta_6 k_{(3-210)}$
$\cdot OH + HCHO \xrightarrow{O_2} HO_2\cdot + CO$	(3-232)	$4.4 \times 10^6 T^{-1}$

Acetaldehyde

$CH_3CHO + h\nu \xrightarrow{O_2} CH_3O_2 + HO_2 + CO$	(3-233)	$\beta_7 k_{(3-210)}$
$\cdot OH + CH_3CHO \xrightarrow{O_2} CH_3CO_3$	(3-234)	$3.0 \times 10^6 T^{-1} e^{250/T}$
$CH_3CO_3 + NO_2 \rightarrow PAN$	(3-235)	$2.1 \times 10^6 T^{-1}$
$PAN \rightarrow CH_3CO_3 + NO_2$	(3-236)	$1.2 \times 10^{18} e^{-13543/T}$
$CH_3CO_3 + NO \xrightarrow{O_2} NO_2 + CH_3CO_2$	(3-237)	$3.1 \times 10^6 T^{-1}$
$CH_3O_2 + NO \rightarrow HCHO + HO_2\cdot + NO_2$	(3-238)	$3.1 \times 10^6 T^{-1}$

Propane

$\cdot OH + PROPANE \rightarrow PO_2$	(3-239)	$6.6 \times 10^6 T^{-1} e^{-680/T}$
$PO_2 + NO \rightarrow HO_2\cdot + NO_2 + CH_3COCH_3$	(3-240)	$3.1 \times 10^6 T^{-1}$

Alkanes

$\cdot OH + Alkane \rightarrow AO_2$ (3-241) $8.0\times10^{6}T^{-1}e^{-560/T}$ (C=4); $6.6\times10^{6}T^{-1}e^{-400/T}$ ($C\geq4$)

$AO_2 + NO \rightarrow 1.3NO_2 - 0.4NO + 0.9HO_2\cdot$ (3-242) $3.1\times10^{6}T^{-1}$ (4)

$+ 0.6CH_3CHO + 0.1RCHO + 0.5MEK$ (C=4)

$\rightarrow 1.7NO_2 - 0.8NO + 0.9HO_2\cdot + 0.15HCHO + 0.3CH_3CHO$

$+ 0.1RCHO + 0.3CH_3COCH_3 + 0.45MEK$ (C>4)

Higher Aldehydes

$\cdot OH + RCHO \xrightarrow{O_2} RCO_3$ (3-243) $9.2\times10^{6}T^{-1}$

$RCO_3 + NO_2 \rightarrow PPN$ (3-244) $2.1\times10^{6}T^{-1}$

$PPN \rightarrow RCO_3 + NO_2$ (3-245) $1.2\times10^{18}e^{-13543/T}$ (5)

$RCO_3 + NO \rightarrow C_2H_5O_2 + NO_2$ (3-246) $3.1\times10^{6}T^{-1}$ (5)

$C_2H_5O_2 + NO \xrightarrow{O_2} CH_3CHO + HO_2\cdot + NO_2$ (3-247) $3.1\times10^{6}T^{-1}$ (5)

$RCHO + h\nu \xrightarrow{O_2} C_2H_5O_2 + CO + HO_2$ (3-248) $\beta_8 k_{(3-210)}$

Ketones

$\cdot OH + MEK \xrightarrow{O_2} XO_2$ (3-249) $4.4\times10^{6}T^{-1}e^{-330/T}$ (6)

$XO_2 + NO \rightarrow NO_2 + CH_3CHO + CH_3CO_3$ (3-250) $3.1\times10^{6}T^{-1}$

$MEK + h\nu \xrightarrow{O_2} CH_3CO_3 + C_2H_5O_2$ (3-251) $\beta_9 k_{(3-210)}$ (4)

$CH_3COCH_3 + h\nu \xrightarrow{O_2} CH_3CO_3 + CH_3O_2$ (3-252) $\beta_{10} k_{(3-210)}$

Alkenes

$$\cdot OH + \text{ethene} \xrightarrow{O_2} 2HCHO + NO_2 - NO + HO_2\cdot \quad (3\text{-}253) \quad 9.7\times10^{5}\,T^{-1}e^{380/T}$$

$$\cdot OH + \text{propene} \xrightarrow{O_2} HCHO + CH_3CHO + HO_2\cdot + NO_2 - NO \quad (3\text{-}254) \quad 1.8\times10^{6}\,T^{-1}e^{540/T}$$

$$\cdot OH + \text{butene} \xrightarrow{O_2} 1.8CH_3CHO + 0.9NO_2 + 0.9HO_2\cdot - NO \quad (3\text{-}255) \quad 5.0\times10^{6}\,T^{-1}e^{540/T}$$

$$O_3 + \text{ethene} \rightarrow HCHO + 0.4\dot{C}H_2O_2 + 0.4CO + 0.12HO_2\cdot \quad (3\text{-}256) \quad 4.2\times10^{3}\,T^{-1}e^{-2560/T}$$

$$O_3 + \text{propene} \rightarrow 0.5HCHO + 0.5CH_3CHO + 0.2CH_2O_2 + 0.2\dot{C}H_3CHOO + 0.3CO + 0.2HO_2\cdot + 0.1\cdot OH + 0.2CH_3O_2 \quad (3\text{-}257) \quad 3.1\times10^{3}\,T^{-1}e^{-1900/T}$$

$$O_3 + \text{butene} \rightarrow CH_3CHO + 0.4\dot{C}H_3CHOO + 0.3HO_2\cdot + 0.2\cdot OH + 0.45CH_3O_2 + 0.2CO \quad (3\text{-}258) \quad 3.3\times10^{3}\,T^{-1}e^{-1050/T}$$

$$\dot{C}H_2O_2 + NO \rightarrow HCHO + NO_2 \quad (3\text{-}259) \quad 3.1\times10^{6}\,T^{-1}$$

$$\dot{C}H_2O_2 + NO_2 \rightarrow HCHO + NO_3 \quad (3\text{-}260) \quad 3.1\times10^{5}\,T^{-1}$$

$$\dot{C}H_2O_2 + SO_2 \rightarrow HCHO + SO_4^{2-} \quad (3\text{-}261) \quad 3.0\times10^{4}\,T^{-1} \quad (7)$$

$$\dot{C}H_2O_2 + H_2O \rightarrow \text{product} \quad (3\text{-}262) \quad 1.5T^{-1}$$

$$CH_3\dot{C}HOO + NO \rightarrow CH_3CHO + NO_2 \quad (3\text{-}263) \quad 3.1\times10^{6}\,T^{-1}$$

$$CH_3\dot{C}HOO + NO_2 \rightarrow CH_3CHO + NO_3 \quad (3\text{-}264) \quad 3.1\times10^{5}\,T^{-1}$$

$$CH_3\dot{C}HOO + SO_2 \rightarrow CH_3CHO + SO_4^{2-} \quad (3\text{-}265) \quad 3.0\times10^{4}\,T^{-1} \quad (7)$$

$$CH_3\dot{C}HOO + H_2O \rightarrow \text{product} \quad (3\text{-}266) \quad 1.5T^{-1}$$

Aromatics

$\cdot OH + Benzene \rightarrow 0.25cresol + 0.25\ HO_2\cdot + 0.65ADD$	(3-267)	$5.3x10x5T^{-1}$	
$\cdot OH + Toluene \rightarrow 0.15ARO_2 + 0.2Cresol + 0.2HO_2\cdot + 0.65ADD$	(3-268)	$2.7x10^6T^{-1}$	
$\cdot OH + Xylene \rightarrow 0.25Cresol + 0.25HO_2\cdot + 0.75ADD$	(3-269)	$7.9x10^6T^{-1}$	
$ADD + NO \rightarrow 0.75NO_2 + 0.75HO_2 + 0.75DIAL + \alpha_1(CHO)_2 + \alpha_2 CH_3COCHO$	(3-270)	$3.1x10^6T^{-1}$	(8)
$\cdot OH + DIAL \rightarrow El$	(3-271)	$1.3x10^7T^{-1}$	(8,9)
$El + NO_2 \rightarrow ElNO_2$	(3-272)	$2.1x10^6T^{-1}$	(9)
$ElNO_2 \rightarrow El + NO_2$	(3-273)	$1.2x10^{18}e^{-13543}/T$	(9)
$El + NO \rightarrow 3NO_2 - 2NO + \alpha_3 HO_2\cdot + \alpha_3(CHO)_2 + \alpha_4 CH_3CO_3 + \alpha_4 CH_3COCHO + \alpha_3 CO$	(3-274)	$3.1x10^6T^{-1}$	
$\cdot OH + (CHO)_2 \xrightarrow{O_2} HO_2\cdot + CO$	(3-275)	$8.8x10^6T^{-1}$	
$(CHO)_2 + h\nu \rightarrow HCHO + CO$	(3-276)	$\beta_{11}k_{(3-210)}$	
$\cdot OH + CH_3COCHO \xrightarrow{O_2} CH_3CO_3 + CO$	(3-277)	$6.6x10^6T^{-1}$	
$CH_3COCHO + h\nu \xrightarrow{O_2} CH_3CO_3 + HO_2\cdot + CO$	(3-278)	$\beta_{12}k_{(3-210)}$	
$\cdot OH + Cresol \rightarrow ADD2$	(3-279)	$1.9x10^7T^{-1}$	(10)
$ADD2 + NO \rightarrow 0.75NO_2 + 0.75HO_2\cdot + 0.75DIAL$	(3-280)	$3.1x10^6T^{-1}$	(10)
$NO_3 + Cresol \rightarrow HNO_3 + Phenoxy$	(3-281)	$6.6x10^6T^{-1}$	
$Phenoxy + NO_2 \rightarrow$ products (o,p-nitrophenols)	(3-282)	$6.6x10^6T^{-1}$	
$ARO_2 + NO \rightarrow 0.75NO_2 + 0.75HO_2\cdot + 0.75ARCHO$	(3-283)	$3.1x10^6T^{-1}$	
$ARCHO + h\nu \rightarrow$ products	(3-284)	$\beta_{13}k_{(3-210)}$	

$\cdot OH + ARCHO \xrightarrow{O_2} ARCO_3$	(3-285)	$5.7\times10^{6}T^{-1}$	
$ARCO_3 + NO_2 \rightarrow PBZN$	(3-286)	$2.1\times10^{6}T^{-1}$	
$PBZN \rightarrow ARCO_3 + NO_2$	(3-287)	$1\times10^{17}e^{-13025/T}$	
$ARCO_3 + NO \rightarrow PhO_2 + NO_2$	(3-288)	$3.1\times10^{6}T^{-1}$	
$PhO_2 + NO \rightarrow Phenoxy + NO_2$	(3-289)	$3.1\times10^{6}T^{-1}$	
Sulfur Dioxide			
$SO_2 + \cdot OH \xrightarrow{M} SO_4^{2-}$	(3-290)	$1.5\times10^{13}T^{-4}$	(7)
Chamber dependent reactions			
$? \rightarrow \cdot OH$	(3-291)	1.5×10^{-4}	(11)
$O_3 \rightarrow$ Wall	(3-292)	1.7×10^{-3}	(11)
General Dilution			(11)

a Units $ppm^{-1}\,min^{-1}$ unless otherwise indicated.

$\beta_i k_{(3-210)}$ is normally experimentally determined for smog chamber simulations. Values of $(\beta_i k_{(3-210)})$ can be computed independently using literature absorption cross-sections and light intensity and wavelength distributions; or β_i can be calculated for a typical distribution.

1 $cm^3\,molecule^{-1}\,s^{-1}$

2 min^{-1}

3 Chamber dependent, a heterogeneous reaction.

4 MEK = $CH_3CH_2COCH_3$

5 RCHO = CH_3CH_2CHO; PPN = peroxypropionylnitrate

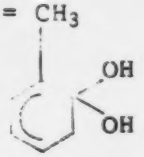
6 $XO_2 = CH_3\underset{\underset{OO}{|}}{C}HCOCH_3$

7 SO_4^{2-} is sulfate, presumed to be sulfuric acid aerosol.

8 DIAL = CHCOCH = CHCHO

9 E1 = RCOCH $=\!=$ CR'CO_3

10 ADD2 = CH_3



11 Chamber dependent.

the literature is the method used to describe hydrocarbon chemistry. Development of a concise and uniform way of defining the reactions of hydrocarbons with other atmospheric pollutants is difficult due to the large number of species and reactions involved. In contrast to the organic chemistry, the reactions used to describe atmospheric inorganic chemistry, ie, those reactions involving O_3, SO_2, etc, are quite well established and vary little from model to model. Only one model, the Carbon Bond Mechanism/19/, presents a consistent approach to the modelling of the reactions of organic atmospheric pollutants. In this system, the carbon bond rather than the molecule is treated as the principal unit of reaction. The mechanism was based on the assumption that analogously bonded carbon atoms react similarly and independently of the molecules in which they occur. The validation results are very good, however the model neglects the contribution of SO_2 to photochemical smog formation.

The Hecht-Seinfeld-Dodge model/16/, (H-S-D), was based on the grouping of the large number of hydrocarbons involved in photochemical smog formation by class, ie, paraffin, olefin, etc. However, in order for the mechanism to be of use in analyzing complex mixtures of hydrocarbons, the classes must be subdivided according to the reactivity of the component hydrocarbons with $\cdot OH$. The mechanism was not consistent in its approach to the grouping of hydrocarbons and required the use of many stoichiometric coefficients to define the reactions. The model was not tested to determine its ability to model the reactions of a complicated mixture of hydrocarbons.

The Atmospheric Model for Sulfur/18/, ATMOS, was the first photochemical model to include the reactions of SO_2. However the description of the hydrocarbon chemistry was based on the Hecht-Seinfeld-Dodge Mechanism/16/. Validation results suggested a deficiency in its treatment of SO_2 chemistry. The Surrogate Chemical Mechanism, SCHEME/17/, a simplified, more efficient version of ATMOS, could only model photochemical smog formation as well as ATMOS.

The Atkinson mechanism/22/ is the most recent addition to the number of photochemical models reported in the literature. In this mechanism hydrocarbons are separated into a number of classes based predominantly on $\cdot OH$ rate constants. Validation results suggested that the model accurately simulates photochemical smog formation. As is the case with the Carbon Bond Mechanism, Atkinson's model is very long and requires considerable computing time.

The Carbon Bond Mechanism/19/ is recommended as the basis from which to develop a photochemical model capable of simulating the reactions of the emissions from Ontario Hydro's fossil fuel fired

generating stations. The selection is based on the fact that the CBM presents the most consistent method for handling hydrocarbon chemistry. It does not arbitrarily eliminate hydrocarbons, ie, CH_4, acetone, benzene, etc, and there are very few exceptions to the rules employed in the classification of hydrocarbons. The mechanism was developed to model the chemistry of a hydrocarbon rich atmosphere and it lacks the reactions necessary to define SO_2 chemistry. However, as can be seen from the other photochemical models presented, the number of reactions used to describe SO_2 chemistry is small and these reactions can readily be incorporated into the CBM. Testing of the Carbon Bond Mechanism with data collected from previous Hydro field studies of plume chemistry may suggest further modifications. The tailoring of this model to meet Hydro's needs and its application will be discussed in the next section.

4.0 A PHOTOCHEMICAL MODEL BASED ON THE CARBON BOND MECHANISM-III

The reactions selected to comprise a photochemical model capable of simulating the chemistry of the emissions from Ontario Hydro's fossil fuel fired generating stations are listed in Table 4.1. The majority of these reactions was taken from the Carbon Bond Mechanism-III presented in Table 3.3. The mechanism is supplemented with a reaction which describes the atmospheric chemistry of SO_2, equation 4-1.

$$SO_2 + \cdot OH \rightarrow SULF \qquad k = 1.77 \times 10^3 \ ppm^{-1} min^{-1}$$

$$(SULF = H_2SO_4) \qquad T = 298°K, \ 1 \ atm \ P \qquad (4\text{-}1)$$

This reaction, addition of the hydroxyl radical to SO_2, is believed to be the dominant path for SO_2 oxidation in the atmosphere (see section 2.4). The contribution of other chemical species present in the polluted atmosphere, ie, $HO_2\cdot$ and $RO_2\cdot$, to SO_2 oxidation is considered questionable and these reactions were therefore not included. The recommended reaction rate constants are given in parentheses.

The reactions listed in Table 4.1 can be written as first order differential equations in which the change in concentration of the reacting components, intermediates and products is expressed with respect to a change in time. The HAVCHM computer program was selected to integrate the differential equations and present the results, the changes in concentration of reactants and products as a function of time, in the form of graphs and/or tables. The HAVCHM algorithm is based on the Gear integration technique and the use of this program is described in "A User's Guide to HAVCHM", Ontario Hydro Report No C82-126-K/23/.

The Carbon Bond Mechanism-III was originally run using the computer program CHEMK/20/. The first step in the testing of the photochemical model, Table 4.1, based largely on CBM-III, was to confirm that this model, when run using the HAVCHM program, is able to duplicate the results obtained with the CBM-III using the CHEMK program. An attempt was therefore made to repeat the validation simulations provided by Killus and Whitten in the manual describing the CBM-III/19/. The validation runs involved simulating the chemical reactions observed in a NO_x-hydrocarbon filled smog chamber. The details and results of the experiments are presented in Appendix A. The simulation of smog chamber experiments required a slight modification of the photochemical model. Reactions describing the loss of chemical reactants to the chamber walls were incorporated into the mechanism, see Appendix A.

The photochemical model, Table 4.1, and the HAVCHM program were able to successfully reproduce the results obtained by Killus and Whitten using the CBM-III/19/ and the experimental data collected from the smog chambers. It must however be emphasized that care is required in the selection of the reaction rate constants. Small changes, especially in the photolysis rate constants, cause large differences in the appearance of the concentration versus time profiles. Note also that the hydrocarbon group concentrations, ie, OLE, PAR, ARO etc., were entered using ppm units.

The next step in the validation of the model was to test its ability to simulate the chemistry of a NO_x-hydrocarbon-SO_2 polluted atmosphere. A preliminary study was carried out using the results of a smog chamber study reported by D.F. Miller/24/. The details and results of this validation run are presented in Appendix B. Again, reactions accounting for the loss of chemical reactants to the chamber walls were added to the model. The experimental results of the smog chamber study are also presented in Appendix B. The fit between experimental data and the data generated by the model was within ±8% of the experimental values for $[NO_2]_{max}$, ±23% of the experimental values for $[O_3]_{max}$ and ±55% for sulfate % yield. The experimental values have however been corrected for chamber dilution, while the calculated values have not. With such a correction factor, it should be possible to get better agreement. These results suggest that further refinement of the model is required, perhaps a more careful consideration of the heterogeneous smog chamber dependent reactions. Nevertheless, the photochemical model presented in Table 4.1 is ready to be tested for use as a tool to simulate the chemical reactions which occur in a NO_x-hydrocarbon-SO_2 polluted atmosphere. SO_2, NO_x and O_3 concentration data for use in such testing can generally be readily obtained from the literature. Hydrocarbon distribution and concentration data are however more difficult to locate and for this reason a table of

TABLE 4.1

PHOTOCHEMICAL MODEL

Reaction		Rate Constant at 298°K ($ppm^{-1}\,min^{-1}$)
$NO_2 \rightarrow NO + O$	(3-113)	a (0.3)
$O + (O_2) + (M) \rightarrow O_3$	(3-114)	4.40×10^6 b
$NO + O_3 \rightarrow NO_2 + O_2$	(3-115)	26.6
$NO_2 + O_3 \rightarrow NO_3 + O_2$	(3-116)	0.048
$NO_2 + O \rightarrow NO + O_2$	(3-117)	1.3×10^4
$OH + O_3 \rightarrow HO_2 + O_2$	(3-118)	100
$HO_2 + O_3 \rightarrow OH + 2O_2$	(3-119)	2.40
$OH + NO_2 \rightarrow HNO_3$	(3-120)	1.60×10^4
$OH + CO \xrightarrow{O_2} HO_2 + CO_2$	(3-121)	440
$NO + NO + (O_2) \rightarrow NO_2 + NO_2$	(3-122)	1.50×10^{-4} b
$NO + NO_3 \rightarrow NO_2 + NO_2$	(3-123)	2.80×10^4
$NO_2 + NO_3 + H_2O \rightarrow 2HNO_3$	(3-124)	c (1.7×10^{-3})
$NO + HO_2 \rightarrow NO_2 + OH$	(3-125)	1.20×10^4
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	(3-126)	1.50×10^4
$X + PAR \rightarrow$	(3-127)	10^5
$OH + PAR \xrightarrow{O_2} MEO_2 + H_2O$	(3-128)	1300
$O + OLE \xrightarrow{O_2} MEO_2 + ACO_3 + X$	(3-129)	2700
$O + OLE \rightarrow CARB + PAR$	(3-130)	2700
$OH + OLE \xrightarrow{O_2} RAO_2$	(3-131)	3.70×10^4

O_3 + OLE → CARB + CRIG	(3-132)	0.008
O_3 + OLE $\xrightarrow{O_2}$ CARB + MCRG + X	(3-133)	0.008
O + ETH $\xrightarrow{O_2}$ MEO_2 + HO_2 + CO	(3-134)	600
O + ETH → CARB + PAR	(3-135)	600
OH + ETH $\xrightarrow{O_2}$ RBO_2	(3-136)	1.20×10^4
O_3 + ETH → CARB + CRIG	(3-137)	0.0024
NO + ACO_3 $\xrightarrow{O_2}$ NO_2 + MEO_2	(3-138)	1.04×10^4
NO + RBO_2 $\xrightarrow{O_2}$ NO_2 + CARB + HO_2 + CARB	(3-139)	1.20×10^4
NO + RAO_2 $\xrightarrow{O_2}$ NO_2 + CARB + HO_2 + CARB	(3-140)	1.20×10^4
NO + MEO_2 $\xrightarrow{O_2}$ NO_2 + CARB + MEO_2 + X	(3-141)	3800
NO + MEO_2 $\xrightarrow{O_2}$ NO_2 + CARB + HO_2	(3-142)	7700
NO + MEO_2 → NRAT	(3-143)	500[d]
O_3 + RBO_2 → CARB + CARB + HO_2 + O_2	(3-144)	5.0
O_3 + RAO_2 → CARB + CARB + HO_2 + O_2	(3-145)	200
OH + CARB → CRO_2 + X	(3-146)	1000
OH + CARB $\xrightarrow{O_2}$ HO_2 + CO	(3-147)	7000
OH + CARB $\xrightarrow{O_2}$ ACO_3 + X	(3-148)	6000
CARB → CO + H_2	(3-149)	$(=0.002\ K_{(3-113)}^{[a]}$ (1.9×10^{-4})
CARB + (O_2) $\xrightarrow{O_2}$ 2/3 ($2HO_2$ + CO) 1/3 ($2MEO_2$ + CO + 2X)	(3-150)	$(=0.002\ K_{(3-113)}^{[a]}$ (3.8×10^{-4})

$NO_2 + ACO_3 \rightarrow PAN$	(3-151)	7000
$PAN \rightarrow ACO_3 + NO_2$	(3-152)	0.022
$HO_2 + ACO_3 \rightarrow$ Stable Products	(3-153)	1.50×10^4
$HO_2 + MEO_2 \rightarrow$ Stable Products	(3-154)	9000
$NO + CRIG \rightarrow NO_2 + CARB$	(3-155)	1.20×10^4
$NO_2 + CRIG \rightarrow NO_3 + CARB$	(3-156)	8000
$CARB + CRIG \rightarrow$ Ozonide	(3-157)	2000
$NO + MCRG \rightarrow NO_2 + CARB + PAR$	(3-158)	1.20×10^4
$NO_2 + MCRG \rightarrow NO_3 + CARB + PAR$	(3-159)	8000
$CARB + MCRG \rightarrow$ Ozonide	(3-160)	2000
$CRIG \rightarrow CO + H_2O$	(3-161)	670[e]
$CRIG \rightarrow$ Stable Products	(3-162)	240[e]
$CRIG \xrightarrow{O_2} HO_2 + HO_2 + CO$	(3-163)	90[e]
$MCRG \rightarrow$ Stable Products	(3-164)	150[e]
$MCRG \xrightarrow{O_2} MEO_2 + OH + CO$	(3-165)	340[e]
$MCRG \xrightarrow{O_2} MEO_2 + HO_2$	(3-166)	425[e]
$MCRG \xrightarrow{O_2} CARB + HO_2 + CO + HO_2$	(3-167)	85[e]
$OH + ARO \xrightarrow{O_2} RARO + H_2O$	(3-168)	6000
$OH + ARO \xrightarrow{O_2} HO_2 + OPEN$	(3-169)	1.45×10^4
$NO + RARO \xrightarrow{O_2} NO_2 + PHEN + HO_2$	(3-170)	4000
$OPEN + NO \xrightarrow{O_2} NO_2 + DCRB + X + APRC$	(3-171)	6000

$APRC \xrightarrow{O_2} DCRB + CARB + CO$	(3-172)	10^4 e
$APRC \xrightarrow{O_2} CARB + CARB + CO + CO$	(3-173)	10^4 e
$PHEN + NO_3 \rightarrow PHO + HNO_3$	(3-174)	5000
$PHO + NO_2 \rightarrow NPHN$	(3-175)	4000
$PHO + HO_2 \rightarrow PHEN + O_2$	(3-176)	5.00×10^4
$OPEN + O_3 \rightarrow DCRB + X + APRC$	(3-177)	40
$OH + PHEN \xrightarrow{O_2} HO_2 + APRC + PAR + CARB$	(3-178)	3.00×10^4
$DCRB \xrightarrow{O_2} 1/2\ (HO_2 + ACO_3 + CO)$ $1/2\ (MEO_2 + HO_2 + 2CO)$	(3-179)	$(\approx 0.04\ K_{(3-113)})$ a (1.35×10^{-2})
$PHEN + OH \rightarrow PHO$	(3-180)	10^4
$CRO_2 + NO \xrightarrow{O_2} NO_2 + HO_2 + DCRB$	(3-181)	1.20×10^4
$HONO \rightarrow OH + NO$	(3-182)	$(\approx 0.06\ K_{(3-113)})$ a (1.8×10^{-2})
$OH + NO \rightarrow HONO$	(3-183)	9770
$O_3 \rightarrow O^{1}D$	(3-184)	$(\approx 10^{-3}\ K_{3-113})$ a (0.0)
$O^{1}D + (\underset{\downarrow}{M})\ O$	(3-185)	4.44×10^{10}
$O^{1}D + H_2O \rightarrow OH + OH$	(3-186)	3.4×10^5
$SO_2 + OH \rightarrow SULF$	(4-1)	1.77×10^3

a Sunlight-dependent; units of min^{-1}.
b Units of $ppm^{-2}\ min^{-1}$.
c Heterogeneous; pseudo third order. Equal to 591 x k(N_2O_5 + H_2O)
d The rate of nitrate formation varies according to the hydrocarbon composition. Killus and Whitten/19/ recommend the default value of 500 $ppm^{-1}\ min^{-1}$. This was found to be the best value for a hydrocarbon mixture whose paraffin content most closely resembles that of urban environments.
e Units of min^{-1}.

typical hydrocarbon concentrations detected in urban and rural air is presented in Appendix C/25/. The results of testing the photochemical model with emissions data collected from Ontario Hydro's fossil fuel fired qenerating stations will be presented in a subsequent report.

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APPENDIX A

Two validation simulations of the chemical reactions which occur in a NO_x-hydrocarbon filled smog chamber are described. The data were taken from the CBM-III manual prepared by Killus and Whitten/19/. The hydrocarbon fractions contained varying amounts of olefins, paraffins and aromatics. The mixture of hydrocarbons was different for the two runs and the rate of nitrate formation, reaction 3-143, which is dependent upon hydrocarbon composition, was assigned the value 500 $ppm^{-1} min^{-1}$ for run No 231, and 250 $ppm^{-1} min^{-1}$ for run No 247.

The following rate constants were used for the photolysis reactions:

$$k_{(3-113)} = 0.3 \text{ min}^{-1}$$

$$k_{(3-149)} = 1.9 \times 10^{-4} \text{ min}^{-1}$$

$$k_{(3-150)} = 3.8 \times 10^{-4} \text{min}^{-1}$$

$$k_{(3-179)} = 1.35 \times 10^{-2} \text{min}^{-1}$$

$$k_{(3-184)} = 0.0 \text{ min}^{-1}$$

Reactions 4-2 and 4-3 were added to describe the loss of chemical reactants to the walls of the smog chamber.

$$O_3 \rightarrow \text{LOSS} \qquad k = 1.6 \times 10^{-3} \text{ min}^{-1} \qquad (4\text{-}2)$$

$$NO_2 \rightarrow \text{LOSS} \qquad k = 1.6 \times 10^{-3} \text{ min}^{-1} \qquad (4\text{-}3)$$

The smog chamber dependent conversion of NO_2 and NO_3 to nitric acid, reaction 3-124, was assigned the rate of 1.7×10^{-3} min^{-1}.

Use of the HAVCHM computer program to integrate the first order differential equations required modification of the form of some of the chemical reactions. To illustrate, reaction 3-150 involves one species, CARB, which in the presence of O_2 yields $HO_2\cdot$, CO, MEO_2, CO and X.

$$\text{CARB} + (O_2) \xrightarrow{O_2} 2/3\ (2HO_2 + CO) \qquad (3\text{-}150)$$

$$1/3\ (MEO_2 + CO + 2X)$$

$$k = 3.8 \times 10^{-4} \text{ min}^{-1}$$

The HAVCHM program can however only accommodate 3 reactants and 3 products. The reaction was therefore entered as shown:

	Rate Constant (min^{-1}) at 298°K
CARB → HO_2 + HO_2 + CO	$2/3[k_{(3-150)}]$
CARB → MEO_2 + MEO_2 + A_2	$1/3[k_{(3-150)}]$
A2 → CO + X + X	1×10^6

Reaction 3-179 was treated similarly.

$$DCRB \xrightarrow{O_2} 1/2\ (HO_2 + ACO_3 + CO) \quad 1/2\ (MEO_2 + HO_2 + 2CO) \qquad (3\text{-}179)$$

$k = 1.35 \times 10^{-2}\ min^{-1}$

In the reaction list of the HAVCHM program, reaction 3-179 appears as follows:

	Rate Constant (min^{-1}) at 298°K
DCRB → HO_2 + ACO_3 + CO	$1/2[k_{(3-179)}]$
DCRB → MEO_2 + HO_2 + A7	$1/2[k_{(3-179)}]$
A7 → CO + CO	1×10^6

The initial hydrocarbon/NO_x concentrations for runs 231 and 247 are listed in Table A.1. Table A.2 presents the hydrocarbon group concentrations as entered into the HAVCHM computer program. Copies of the HAVCHM computer printouts including the reaction lists, initial concentrations, reaction rate constants and the tables and plots of species concentration as a function of time, for both simulation runs follow. Note the reaction numbers in the HAVCHM program are not the same as those used in the main text. A summary of the experimental results of the smog chamber study and the results obtained with the photochemical model, Table 4.1, and the CBM-III is presented in Table A.3. Species concentration versus time profiles of the experimental results of the smog chamber studies and those results obtained by Killus and Whitten using the CBM-III are shown in Figures A.1 and A.2.

TABLE A.1

INITIAL HYDROCARBON/NO_x CONCENTRATION DATA

Run No. / Reactant	231 Concentration (ppm)	247 Concentration (ppm)
Ethylene	1.051	1.025
Propylene	0.108	0.054
trans-2-Butene	0.055	0.053
n-Butane	1.130	0.273
2,3-Dimethylbutane	0.715	0.080
Toluene	0.121	0.145
m-Xylene	0.108	0.145
HCHO	0.020	0.003
NO	0.440	0.380
NO_2	0.052	0.125
HONO	0.006	0.005
H_2O	1.7×10^4	1.7×10^4
CO	1.63	1.63

TABLE A.2

HYDROCARBON GROUP CONCENTRATIONS

Run No. / Hydrocarbon Group	231 Concentration (ppm)	247 Concentration (ppm)
PAR	9.365	2.167
OLE	0.108	0.054
CARB	0.13	0.109
ETH	1.051	1.051
ARO	0.229	0.29

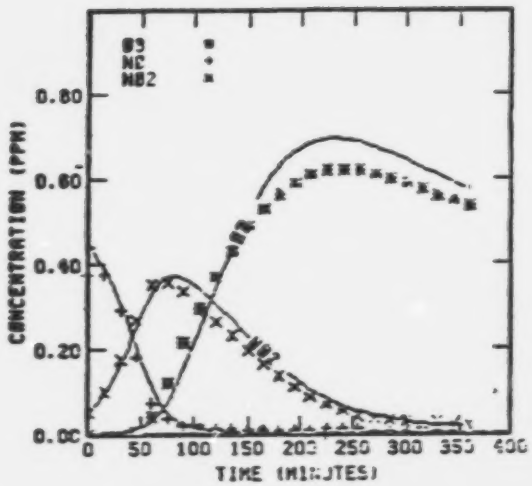
TABLE A.3

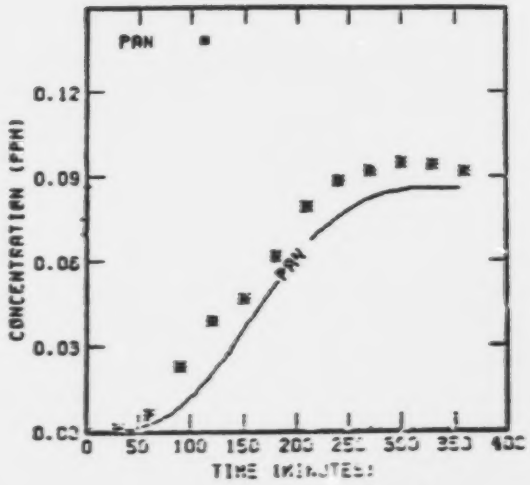
A COMPARISON OF THE EXPERIMENTAL RESULTS OF THE SMOG CHAMBER (SC) STUDIES WITH THE RESULTS CALCULATED USING THE PHOTOCHEMICAL MODEL (PM) AND THE CARBON BOND MECHANISM-III (CBM-III)

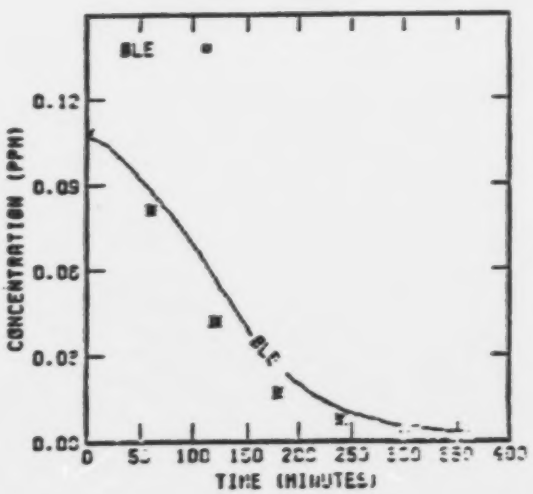
	231 (PC)	231 (PM)	231 (CBM-III)[a]	247 (SC)	247 (PM)	247 (CBM-III)[b]
$NO_{2\ max}$ (ppm)	0.357	0.384	0.375	0.369	0.379	0.375
at time (min)	75	80	75	60	80	80
$O_{3\ max}$ (ppm)	0.623	0.766	0.70	0.657	0.711	0.65
at time (min)	225-255	230	225	210-240	220	225
$O_{3\ 6h}$ (ppm)	0.540	0.620	0.580	-	0.551	-
PAN_{max} (ppm)	0.095	0.123	0.087	0.106	0.150	0.108
at time (min)	270-330	360	310-350	300	340	300
PAN_{6h} (ppm)	0.092	0.123	0.087	-	0.149	-

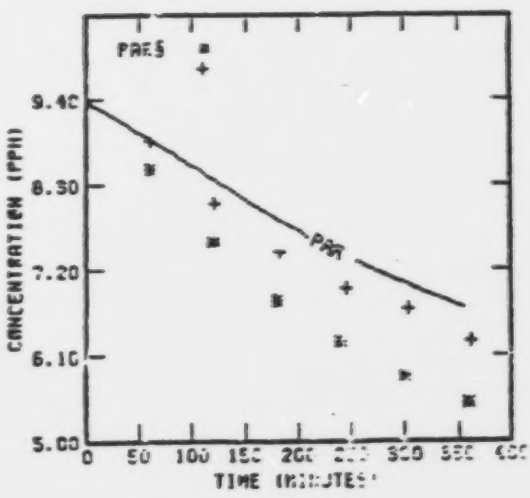
a Values taken from plots shown in Figure A.1.

b Values taken from plots shown in Figure A.2.



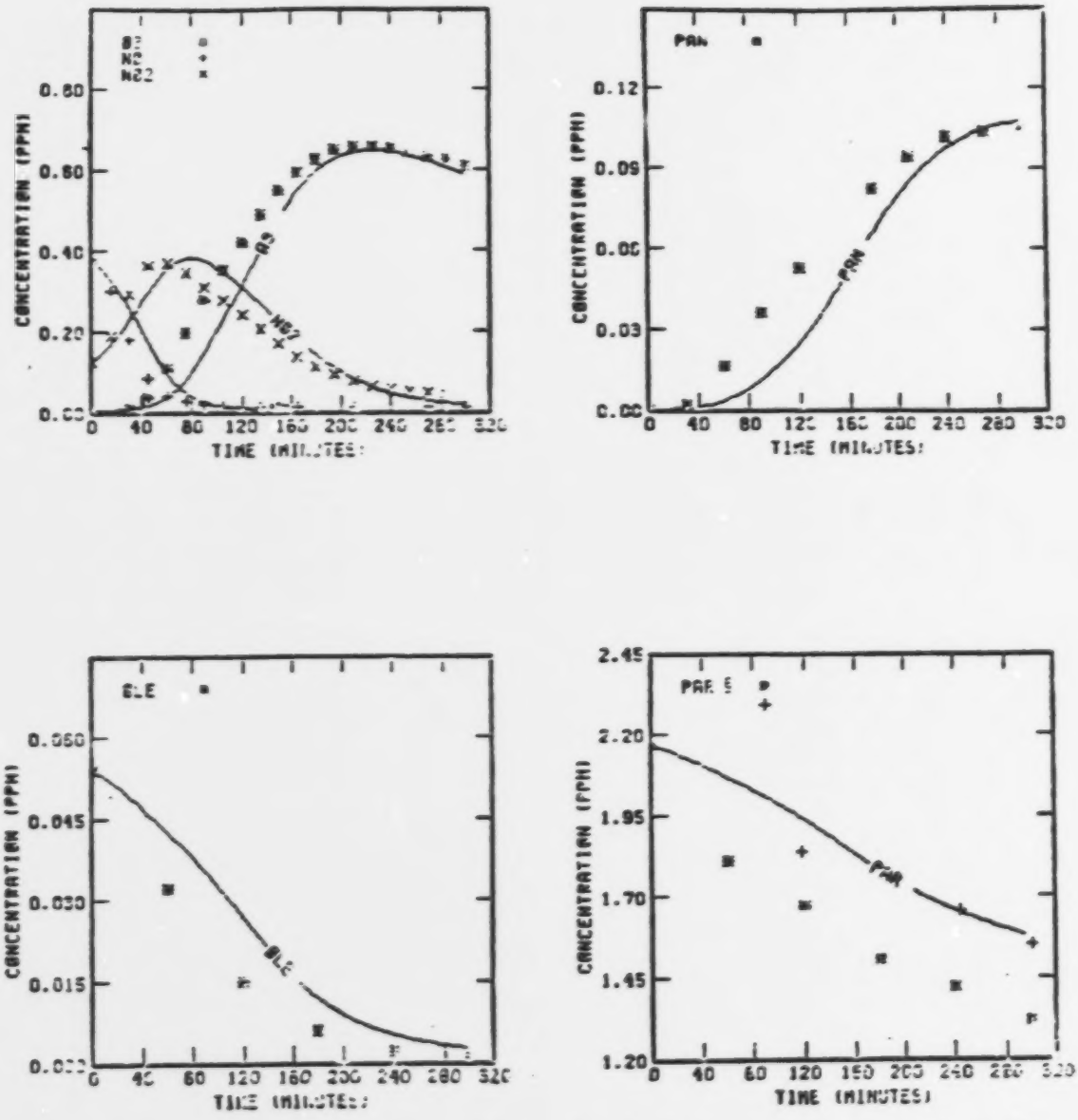






$ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

FIGURE A.1
SIMULATION RESULTS FOR 231/19/
RESULTS OBTAINED WITH THE CBM-III(-)



§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

FIGURE A.2
SIMULATION RESULTS 247/19/.
RESULTS OBTAINED WITH THE CBM-III (-)

HAVCHM VERIFICATION OF CBM-III , RUN 231

ERROR TEST CONSTANT FOR DIFSUB 1.000-008
MINIMUM STEP SIZE 1.000-012
MAXIMUM STEP SIZE ..... 1.500+001
UPPER TIME LIMIT TO INTEGRATE ..... 4.000+002

...FIRST 0 MEMBERS OF SPECIES LIST ARE PRINTED OUT AFTER EACH 0 ITERATION.

...ONLY 6 SPECIES ARE TO BE PRINTED ON PREDEFINED TIME INTERVALS

...DIFSUB METHOD IS 2

...OUTPUT REQUESTED EVERY 1.000+001 TIME UNITS FOR THE FOLLOWING SPECIES :
OLE NO2 NO O3 PAN PAR

1. REACTION LIST

1	NO2	+		+	-> NO	+ O		+
2	O	+		+	-> O3	+		+
3	NO	+ O3		+	-> NO2	+		+
4	NO2	+ O3		+	-> NO3	+		+
5	NO2	+ O		+	-> NO	+		+
6	OH	+ O3		+	-> HO2	+		+
7	HO2	+ O3		+	-> OH	+		+
8	OH	+ NO2		+	-> HNO3	+		+
9	OH	+ CO		+	-> HO2	+ CO2		+
10	NO	+ NO		+	-> NO2	+ NO2		+
11	NO	+ NO3		+	-> NO2	+ NO2		+
12	NO2	+ NO3	+ H2O		-> HNO3	+ HNO3		+
13	NO	+ HO2		+	-> NO2	+ OH		+
14	HO2	+ HO2		+	-> H2O2	+		+
15	X	+ PAR		+	-> SP	+		+
16	OH	+ PAR		+	-> MEO2	+ H2O		+

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17	O	+ OLE	+	-> MEO2	+ ACO3	+ X				
18	O	+ OLE	+	-> CARB	+ PAR	+				
19	OH	+ OLE	+	-> RAO2	+	+				
20	O3	+ OLE	+	-> CARB	+ CRIG	+				
21	OLE	+ O3	+	-> CARB	+ MCRG	+ X				
22	ETH	+ O	+	-> MEO2	+ HO2	+ CO				
23	ETH	+ O	+	-> CARB	+ PAR	+				
24	OH	+ ETH	+	-> RBO2	+	+				
25	O3	+ ETH	+	-> CARB	+ CRIG	+				
26	NO	+ ACO3	+	-> NO2	+ MEO2	+				
27	NO	+ RBO2	+	-> A1	+ HO2	+ CARB				
28	NO	+ RAO2	+	-> A1	+ HO2	+ CARB				
29	NO	+ MEO2	+	-> A1	+ MEO2	+ X				
29A	A1	+	+	-> CARB	+ NO2	+				
30	NO	+ MEO2	+	-> NO2	+ CARB	+ HO2				
31	NO	+ MEO2	+	-> NRAT	+	+				
32	O3	+ RBO2	+	-> CARB	+ HO2	+ CARB				
33	O3	+ RAO2	+	-> CARB	+ HO2	+ CARB				
34	OH	+ CARB	+	-> CRO2	+ X	+				
35	OH	+ CARB	+	-> HO2	+ CO	+				
36	OH	+ CARB	+	-> ACO3	+ X	+				
37	CARB	+	+	-> H2	+ CO	+				
38	CARB	+	+	-> HO2	+ HO2	+ CO				
38A	CARB	+	+	-> MEO2	+ MEO2	+ A2				
38B	A2	+	+	-> CO	+ X	+ X				
39	NO2	+ ACO3	+	-> PAN	+	+				
40	PAN	+	+	-> ACO3	+ NO2	+				
41	HO2	+ ACO3	+	-> SP	+	+				

42	HO2	+ MEO2	+	-> SP	+		+				
43	NO	+ CRIG	+	-> NO2	+ CARB		+				
44	NO2	+ CRIG	+	-> NO3	+ CARB		+				
45	CARB	+ CRIG	+	-> OZNID	+		+				
46	NO	+ MCRG	+	-> NO2	+ CARB		+ PAR				
47	NO2	+ MCRG	+	-> NO3	+ CARB		+ PAR				
48	CARB	+ MCRG	+	-> OZNID	+		+				
49	CRIG	+	+	-> CO	+ H2O		+				
50	CRIG	+	+	-> SP	+		+				
51	CRIG	+	+	-> HO2	+ HO2		+ CO				
52	MCRG	+	+	-> SP	+		+				
53	MCRG	+	+	-> MEO2	+ OH		+ CO				
54	MCRG	+	+	-> MEO2	+ HO2		+				
55	MCRG	+	+	-> CARB	+ HO2		+ A3				
55A	A3	+	+	-> CO	+ HO2		+				
56	OH	+ ARO	+	-> RARO	+ H2O		+				
57	OH	+ ARO	+	-> HO2	+ OPEN		+				
58	NO	+ RARO	+	-> NO2	+ PHEN		+ HO2				
59	OPEN	+ NO	+	-> NO2	+ DCRB		+ A4				
59A	A4	+	+	-> X	+ APRC		+				
60	APRC	+	+	-> DCRB	+ CARB		+ CO				
61	APRC	+	+	-> CARB	+ CO		+ A5				
61A	A5	+	+	-> CARB	+ CO		+				
62	PHEN	+ NO3	+	-> PHO	+ HNO3		+				
63	PHO	+ NO2	+	-> NPHN	+		+				
64	PHO	+ HO2	+	-> PHEN	+		+				
65	OPEN	+ O3	+	-> DCRB	+ X		+ APRC				
66	OH	+ PHEN	+	-> A6	+ HO2		+ APRC				
66A	A6	+	+	-> PAR	+ CARB		+				

67	DCRB	+		+	-> HO2	+	AC03	+	CO	
67A	DCRB	+		+	-> ME02	+	HO2	+	A7	
67B	A7	+		+	-> CO	+	CO	+		
68	PHEN	+	OH	+	-> PHO	+		+		
69	CR02	+	NO	+	-> NO2	+	HO2	+	DCRB	
70	HONO	+		+	-> OH	+	NO	+		
71	OH	+	NO	+	-> HONO	+		+		
72	03	+		+	-> 01D	+		+		
73	01D	+		+	-> O	+		+		
74	01D	+	H20	+	-> OH	+	OH	+		
75	S02	+	OH	+	-> SULF	+		+		
76	03	+		+	-> LOSS	+		+		
77	HO2	+		+	-> LOSS	+		+		

2. SPECIES LABELS READ AS INPUT

NO2	NO	O	03	H20	OH	NO3	HO2	HNO3	CO
C02	H202	X	PAR	ME02	OLE	AC03	CARB	RA02	CRIG
MCRG	ETH	RB02	CR02	H2	NRAT	PAN	SP	OZNID	ARO
RARO	OPEN	PHEN	DCRB	APRC	PHO	NPHN	HONO	01D	A1
A2	A3	A4	A5	A6	A7	S02	SULF	LOSS	

NUMBER OF REACTIONS 86
NUMBER OF SPECIES 49
NUMBER OF SPECIES VARIED 49

3. INITIAL CONCENTRATIONS

NO2	5.2000-002
NO	4.4000-001
O	.0000
03	.0000
H20	1.7000+004
OH	.0000
NO3	.0000
HO2	.0000
HNO3	.0000
CO	1.6300+000
C02	.0000
H202	.0000
X	.0000
PAR	9.3650+000
ME02	.0009

OLE	1.0800-001
ACOS	.0000
CARB	1.3000-001
RAO2	.0000
CRIG	.0000
MCRG	.0000
ETH	1.0510+000
RBO2	.0000
CRO2	.0000
H2	.0000
HRAT	.0000
PAN	.0000
SP	.0000
OZNID	.0000
ARO	2.2900-001
RARO	.0000
OPEN	.0000
PHEN	.0000
DCRB	.0000
APRC	.0000
PHO	.0000
NPHN	.0000
HONO	6.0000-003
O1D	.0000
A1	.0000
A2	.0000
A3	.0000
A4	.0000
A5	.0000
A6	.0000
A7	.0000
SO2	.0000
SULF	.0000
LOSS	.0000

4. REACTION RATE CONSTANTS

1	3.0000-001
2	4.4000+006
3	2.6600+001
4	4.8000-002
5	1.3000+004
6	1.0000+002
7	2.4000+000
8	1.6000+004
9	4.4000+002
10	1.5000-004
11	2.8000+004
12	1.7000-003
13	1.2000+004
14	1.5000+004
15	1.0000+005
16	1.3000+003
17	2.7000+003
18	2.7000+003
19	3.7000+004

68	1.0000+004
69	1.2000+004
70	1.8000-002
71	9.7700+003
72	.0000
73	4.4400+010
74	3.4000+005
75	1.7700+003
76	1.6000-003
77	1.6000-003

HAVCHM VERIFICATION OF CBM-III , RUN 231

TIME - CONCENTRATION REPORT

TIME	OLE	NO2	NO	O3	PAN	PAR
.000	1.0800-001	5.2000-002	4.4000-001	.0000	.0000	9.3650+000
1.000+001	1.0631-001	8.1865-002	4.0767-001	2.2503-003	3.8215-005	9.3552+000
2.000+001	1.0413-001	1.2209-001	3.6359-001	3.7600-003	1.4042-004	9.3422+000
3.000+001	1.0146-001	1.7093-001	3.0920-001	6.1810-003	3.7509-004	9.3260+000
4.000+001	9.8360-002	2.2614-001	2.4648-001	1.0230-002	8.5389-004	9.3066+000
5.000+001	9.4936-002	2.8327-001	1.7974-001	1.7478-002	1.7344-003	9.2847+000
6.000+001	9.1275-002	3.3501-001	1.1622-001	3.1607-002	3.2024-003	9.2611+000
7.000+001	8.7365-002	3.7100-001	6.6343-002	6.0011-002	5.4192-003	9.2364+000
8.000+001	8.3025-002	3.8415-001	3.6972-002	1.0852-001	8.4455-003	9.2107+000
9.000+001	7.8067-002	3.7930-001	2.2478-002	1.7188-001	1.2257-002	9.1834+000
1.000+002	7.2473-002	3.6366-001	1.4930-002	2.4217-001	1.6842-002	9.1541+000
1.100+002	6.6379-002	3.4165-001	1.0510-002	3.1516-001	2.2203-002	9.1226+000
1.200+002	6.0000-002	3.1654-001	7.7025-003	3.8839-001	2.8305-002	9.0893+000
1.300+002	5.3589-002	2.9031-001	5.8345-003	4.5921-001	3.5033-002	9.0549+000
1.400+002	4.7379-002	2.6358-001	4.5412-003	5.2479-001	4.2203-002	9.0202+000
1.500+002	4.1553-002	2.3672-001	3.6089-003	5.8293-001	4.9601-002	8.9863+000
1.600+002	3.6228-002	2.1034-001	2.9135-003	6.3251-001	5.7016-002	8.9537+000
1.700+002	3.1457-002	1.8512-001	2.3808-003	6.7327-001	6.4266-002	8.9229+000
1.800+002	2.7248-002	1.6155-001	1.9639-003	7.0551-001	7.1209-002	8.8943+000
1.900+002	2.3575-002	1.3996-001	1.6318-003	7.2990-001	7.7745-002	8.8679+000
2.000+002	2.0396-002	1.2053-001	1.3637-003	7.4729-001	8.3810-002	8.8437+000
2.100+002	1.7660-002	1.0328-001	1.1449-003	7.5856-001	8.9372-002	8.8217+000
2.200+002	1.5312-002	8.8125-002	9.6470-004	7.6461-001	9.4422-002	8.8018+000
2.300+002	1.3302-002	7.4946-002	8.1527-004	7.6625-001	9.8965-002	8.7837+000
2.400+002	1.1582-002	6.3568-002	6.9065-004	7.6422-001	1.0302-001	8.7673+000
2.500+002	1.0111-002	5.3808-002	5.8628-004	7.5918-001	1.0660-001	8.7524+000
2.600+002	8.8503-003	4.5481-002	4.9857-004	7.5168-001	1.0975-001	8.7388+000
2.700+002	7.7695-003	3.8412-002	4.2472-004	7.4223-001	1.1249-001	8.7265+000
2.800+002	6.8408-003	3.2439-002	3.6250-004	7.3122-001	1.1484-001	8.7152+000
2.900+002	6.0413-003	2.7418-002	3.1011-004	7.1902-001	1.1684-001	8.7049+000
3.000+002	5.3514-003	2.3221-002	2.6611-004	7.0593-001	1.1850-001	8.6954+000
3.100+002	4.7544-003	1.9735-002	2.2933-004	6.9220-001	1.1987-001	8.6865+000
3.200+002	4.2365-003	1.6862-002	1.9880-004	6.7804-001	1.2095-001	8.6783+000
3.300+002	3.7860-003	1.4518-002	1.7372-004	6.6364-001	1.2176-001	8.6706+000
3.400+002	3.3929-003	1.2627-002	1.5339-004	6.4915-001	1.2235-001	8.6634+000
3.500+002	3.0490-003	1.1122-002	1.3722-004	6.3471-001	1.2271-001	8.6565+000
3.600+002	2.7472-003	9.9442-003	1.2465-004	6.2043-001	1.2288-001	8.6499+000
3.700+002	2.4816-003	9.0396-003	1.1518-004	6.0639-001	1.2288-001	8.6436+000
3.800+002	2.2471-003	8.3599-003	1.0834-004	5.9267-001	1.2274-001	8.6374+000
3.900+002	2.0395-003	7.8623-003	1.0370-004	5.7932-001	1.2248-001	8.6315+000

82-483

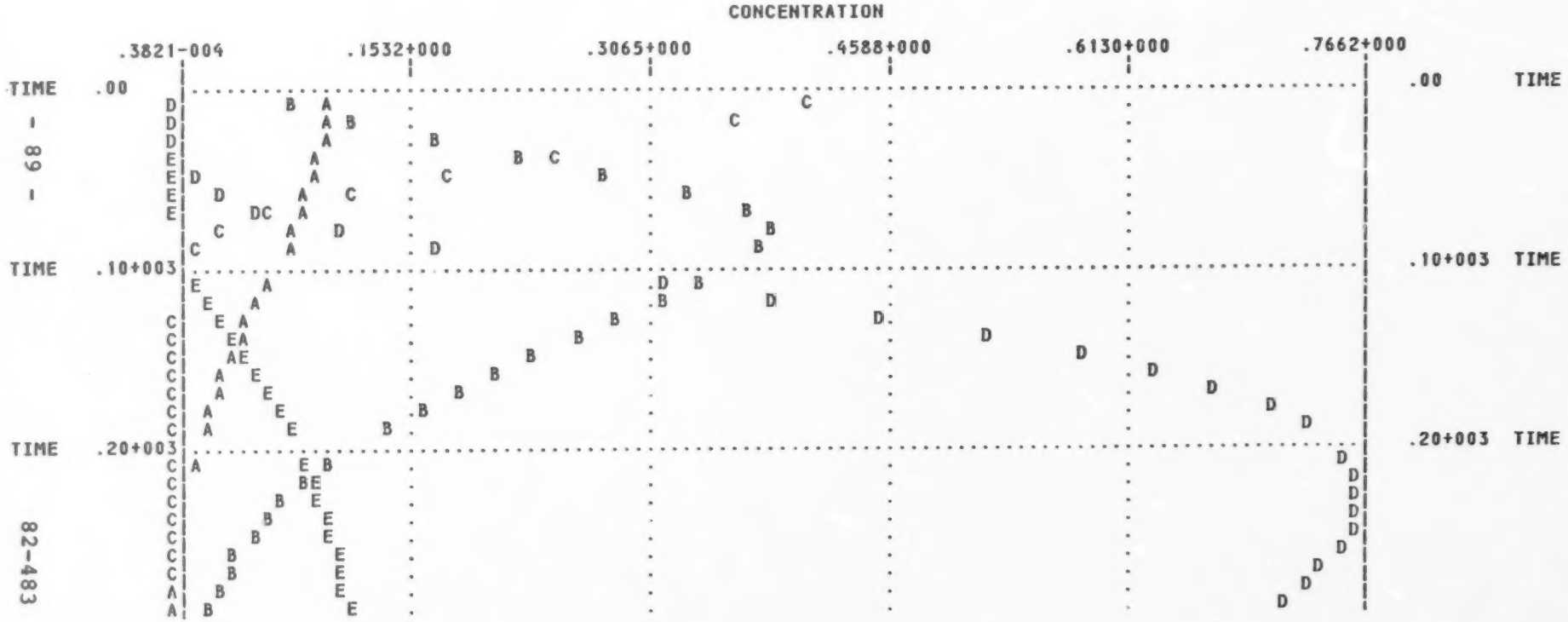
4.000+002 1.8553-003 7.5094-003 1.0086-004 5.6639-001 1.2212-001 8.6256+000

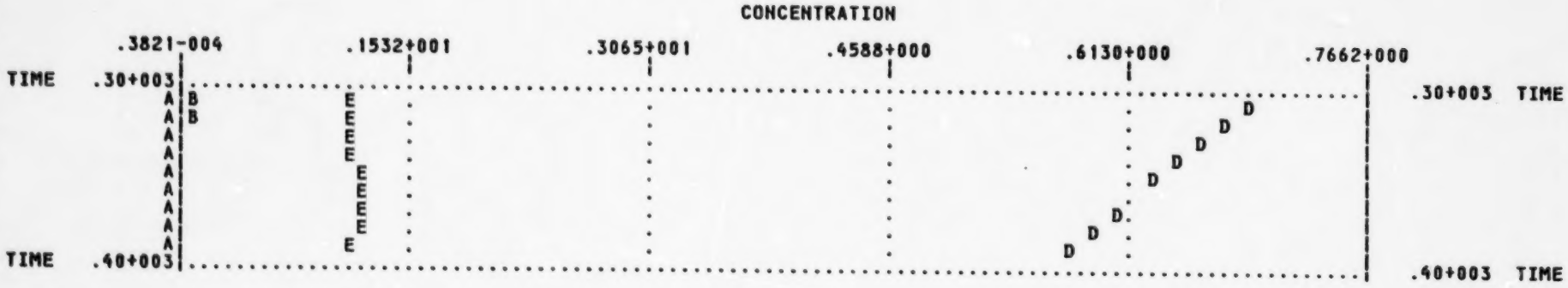
HAVCHM VERIFICATION OF CBM-III , RUN 231

PLOT OF SPECIES

PLOT CODES FOR SPECIES ARE :

A -> OLE B -> NO2 C -> NO D -> O3 E -> PAN




CONCENTRATION
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.1532+001
.3065+001
.4588+000
.6130+000
.7662+000
TIME .30+003
TIME .40+003
.30+003 TIME
.40+003 TIME

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Divide fault occurred: was not checked by program.

Floating point underflow occurred: was not checked by program.

@BRKPT PRINT$
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HAVCHM VERIFICATION OF CBM-III , RUN 247

ERROR TEST CONSTANT FOR DIFSUB 1.000-008
MINIMUM STEP SIZE 1.000-012
MAXIMUM STEP SIZE ..... 1.500+001
UPPER TIME LIMIT TO INTEGRATE ..... 4.000+002

...FIRST 0 MEMBERS OF SPECIES LIST ARE PRINTED OUT AFTER EACH 0 ITERATIONS

...ONLY 6 SPECIES ARE TO BE PRINTED ON PREDEFINED TIME INTERVALS

...DIFSUB METHOD IS 2

...OUTPUT REQUESTED EVERY 1.000+001 TIME UNITS FOR THE FOLLOWING SPECIES :
OLE NO2 NO O3 PAN PAR

1. REACTION LIST

	1	NO2	+		+	-> NO	+ O	+
	2	O	+		+	-> O3	+	+
	3	NO	+	O3	+	-> NO2	+	+
	4	NO2	+	O3	+	-> NO3	+	+
	5	NO2	+	O	+	-> NO	+	+
	6	OH	+	O3	+	-> HO2	+	+
	7	HO2	+	O3	+	-> OH	+	+
	8	OH	+	NO2	+	-> HNO3	+	+
	9	OH	+	CO	+	-> HO2	+ CO2	+
	10	NO	+	NO	+	-> NO2	+ NO2	+
	11	NO	+	NO3	+	-> NO2	+ NO2	+
	12	NO2	+	NO3	+ H2O	-> HNO3	+ HNO3	+
	13	NO	+	HO2	+	-> NO2	+ OH	+
	14	HO2	+	HO2	+	-> H2O2	+	+
	15	X	+	PAR	+	-> SP	+	+
	16	OH	+	PAR	+	-> MEO2	+ H2O	+

17	O	+ OLE	+	-> MEO2	+ ACO3	+ X
18	O	+ OLE	+	-> CARB	+ PAR	+
19	OH	+ OLE	+	-> RAO2	+	+
20	O3	+ OLE	+	-> CARB	+ CRIG	+
21	OLE	+ O3	+	-> CARB	+ MCRG	+ X
22	ETH	+ O	+	-> MEO2	+ HO2	+ CO
23	ETH	+ O	+	-> CARB	+ PAR	+
24	OH	+ ETH	+	-> RBO2	+	+
25	O3	+ ETH	+	-> CARB	+ CRIG	+
26	NO	+ ACO3	+	-> NO2	+ MEO2	+
27	NO	+ RBO2	+	-> A1	+ HO2	+ CARB
28	NO	+ RAO2	+	-> A1	+ HO2	+ CARB
29	NO	+ MEO2	+	-> A1	+ MEO2	+ X
29A	A1	+	+	-> CARB	+ NO2	+
30	NO	+ MEO2	+	-> NO2	+ CARB	+ HO2
31	NO	+ MEO2	+	-> NRAT	+	+
32	O3	+ RBO2	+	-> CARB	+ HO2	+ CARB
33	O3	+ RAO2	+	-> CARB	+ HO2	+ CARB
34	OH	+ CARB	+	-> CRO2	+ X	+
35	OH	+ CARB	+	-> HO2	+ CO	+
36	OH	+ CARB	+	-> ACO3	+ X	+
37	CARB	+	+	-> H2	+ CO	+
38	CARB	+	+	-> HO2	+ HO2	+ CO
38A	CARB	+	+	-> MEO2	+ MEO2	+ A2
38B	A2	+	+	-> CO	+ X	+ X
39	NO2	+ ACO3	+	-> PAN	+	+
40	PAN	+	+	-> ACO3	+ NO2	+
41	HO2	+ ACO3	+	-> SP	+	+

42	HO2	+	ME02	+	->	SP	+		+
43	NO	+	CRIG	+	->	NO2	+	CARB	+
44	NO2	+	CRIG	+	->	NO3	+	CARB	+
45	CARB	+	CRIG	+	->	OZNID	+		+
46	NO	+	MCRG	+	->	NO2	+	CARB	+ PAR
47	NO2	+	MCRG	+	->	NO3	+	CARB	+ PAR
48	CARB	+	MCRG	+	->	OZNID	+		+
49	CRIG	+		+	->	CO	+	H2O	+
50	CRIG	+		+	->	SP	+		+
51	CRIG	+		+	->	HO2	+	HO2	+ CO
52	MCRG	+		+	->	SP	+		+
53	MCRG	+		+	->	ME02	+	OH	+ CO
54	MCRG	+		+	->	ME02	+	HO2	+
55	MCRG	+		+	->	CARB	+	HO2	+ A3
55A	A3	+		+	->	CO	+	HO2	+
56	OH	+	ARO	+	->	RARO	+	H2O	+
57	OH	+	ARO	+	->	HO2	+	OPEN	+
58	NO	+	RARO	+	->	NO2	+	PHEN	+ HO2
59	OPEN	+	NO	+	->	NO2	+	DCRB	+ A4
59A	A4	+		+	->	X	+	APRC	+
60	APRC	+		+	->	DCRB	+	CARB	+ CO
61	APRC	+		+	->	CARB	+	CO	+ A5
61A	A5	+		+	->	CARB	+	CO	+
62	PHEN	+	NO3	+	->	PHO	+	HNO3	+
63	PHO	+	NO2	+	->	NPHN	+		+
64	PHO	+	HO2	+	->	PHEN	+		+
65	OPEN	+	O3	+	->	DCRB	+	X	+ APRC
66	OH	+	PHEN	+	->	A6	+	HO2	+ APRC
66A	A6	+		+	->	PAR	+	CARB	+

67	DCRB	+	+	-> HO2	+	AC03	+	CO		
67A	DCRB	+	+	-> ME02	+	HO2	+	A7		
67B	A7	+	+	-> CO	+	CO	+			
68	PHEN	+ OH	+	-> PHO	+		+			
69	CR02	+ NO	+	-> NO2	+	HO2	+	DCRB		
70	HONO	+	+	-> OH	+	NO	+			
71	OH	+ NO	+	-> HONO	+		+			
72	03	+	+	-> 01D	+		+			
73	01D	+	+	-> O	+		+			
74	01D	+ H20	+	-> OH	+	OH	+			
75	S02	+ OH	+	-> SULF	+		+			
76	03	+	+	-> LOSS	+		+			
77	NO2	+	+	-> LOSS	+		+			

2. SPECIES LABELS READ AS INPUT

NO2	NO	O	03	H20	OH	NO3	HO2	HNO3	CO
C02	H202	X	PAR	ME02	OLE	AC03	CARB	RA02	CRIG
MCRG	ETH	RB02	CR02	H2	HRAT	PAN	SP	OZNID	ARO
RARO	OPEN	PHEN	DCRB	APRC	PHO	NPHN	HONO	01D	A1
A2	A3	A4	A5	A6	A7	S02	SULF	LOSS	

NUMBER OF REAGTIONS 86
NUMBER OF SPECIES 49
NUMBER OF SPECIES VARIED 49

3. INITIAL CONCENTRATIONS

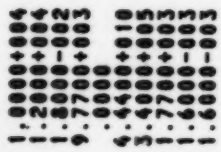
NO2	1.2500-001
NO	3.8000-001
O	.0000
03	.0000
H20	1.7000+004
OH	.0000
NO3	.0000
HO2	.0000
HNO3	.0000
CO	1.6300+000
C02	.0000
H202	.0000
X	.0000
PAR	2.1670+000
ME02	.0000

OLE	5.4000-002
ACO3	.0000
CARB	1.0900-001
RAO2	.0000
CRIG	.0000
MCRG	.0000
ETH	1.0510+000
RBO2	.0000
CRO2	.0000
H2	.0000
HRAT	.0000
PAN	.0000
SP	.0000
OZNID	.0000
ARO	2.9000-001
RARO	.0000
OPEN	.0000
PHEN	.0000
DCRB	.0000
APRC	.0000
PHO	.0000
NPHN	.0000
HONO	5.0000-003
O1D	.0000
A1	.0000
A2	.0000
A3	.0000
A4	.0000
A5	.0000
A6	.0000
A7	.0000
SO2	.0000
SULF	.0000
LOSS	.0000

4. REACTION RATE CONSTANTS

1	3.0000-001
2	4.4000+006
3	2.6600+001
4	4.8000-002
5	1.3000+004
6	1.0000+002
7	2.4000+000
8	1.6000+004
9	4.4000+002
10	1.5000-004
11	2.8000+004
12	1.7000-003
13	1.2000+004
14	1.5000+004
15	1.0000+005
16	1.3000+003
17	2.7000+003
18	2.7000+003
19	3.7000+004

20	8.0000-003
21	8.0000-003
22	6.0000+002
23	6.0000+002
24	1.2000+004
25	2.4000-003
26	1.0400+004
27	1.2000+004
28	1.2000+004
29	3.8000+003
29A	1.0000+006
30	7.7000+003
31	2.5000+002
32	5.0000+000
33	2.0000+002
34	1.0000+003
35	7.0000+003
36	6.0000+003
37	1.9000-004
38	2.5300-004
38A	1.2700-004
38B	1.0000+006
39	7.0000+003
40	2.2000-002
41	1.5000+004
42	9.0000+003
43	1.2000+004
44	8.0000+003
45	2.0000+003
46	1.2000+004
47	8.0000+003
48	2.0000+003
49	6.7000+002
50	2.4000+002
51	9.0000+001
52	1.5000+002
53	3.4000+002
54	4.2500+002
55	8.5000+001
55A	1.0000+006
56	6.0000+003
57	1.4500+004
58	4.0000+003
59	6.0000+003
59A	1.0000+006
60	1.0000+004
61	1.0000+004
61A	1.0000+006
62	5.0000+003
63	4.0000+003
64	5.0000+004
65	4.0000+001
66	3.0000+004
66A	1.0000+006
67	6.7500-003
67A	6.7500-003
67B	1.0000+006



HAVCHM VERIFICATION OF CBM-III , RUN 247

TIME - CONCENTRATION REPORT

TIME	OLE	NO2	NO	O3	PAN	PAR
.000	5.4000-002	1.2500-001	3.8000-001	.0000	.0000	2.1670+000
1.000+001	5.3203-002	1.3894-001	3.6267-001	4.3024-003	6.1382-005	2.1630+000
2.000+001	5.2142-002	1.6344-001	3.3361-001	5.4960-003	1.9216-004	2.1575+000
3.000+001	5.0784-002	1.9564-001	2.9538-001	7.4186-003	4.4895-004	2.1501+000
4.000+001	4.9129-002	2.3506-001	2.4889-001	1.0587-002	9.3126-004	2.1407+000
5.000+001	4.7213-002	2.7940-001	1.9378-001	1.6046-002	1.7953-003	2.1293+000
6.000+001	4.5101-002	3.2378-001	1.3712-001	2.6077-002	3.2532-003	2.1162+000
7.000+001	4.2844-002	3.6015-001	8.6113-002	4.5509-002	5.5365-003	2.1018+000
8.000+001	4.0434-002	3.7931-001	4.9810-002	8.0995-002	8.8128-003	2.0865+000
9.000+001	3.7802-002	3.7924-001	2.9566-002	1.3315-001	1.3125-002	2.0700+000
1.000+002	3.4911-002	3.6526-001	1.8946-002	1.9550-001	1.8473-002	2.0522+000
1.100+002	3.1792-002	3.4209-001	1.2876-002	2.6283-001	2.4889-002	2.0325+000
1.200+002	2.8532-002	3.1340-001	9.0721-003	3.3255-001	3.2489-002	2.0110+000
1.300+002	2.5253-002	2.8255-001	6.5666-003	4.0253-001	4.0985-002	1.9877+000
1.400+002	2.2087-002	2.5167-001	4.8802-003	4.6974-001	5.0416-002	1.9635+000
1.500+002	1.9148-002	2.2149-001	3.7165-003	5.3073-001	6.0376-002	1.9389+000
1.600+002	1.6507-002	1.9249-001	2.8870-003	5.8302-001	7.0492-002	1.9150+000
1.700+002	1.4191-002	1.6531-001	2.2776-003	6.2558-001	8.0421-002	1.8923+000
1.800+002	1.2194-002	1.4049-001	1.8182-003	6.5846-001	8.9893-002	1.8711+000
1.900+002	1.0491-002	1.1833-001	1.4644-003	6.8238-001	9.8725-002	1.8517+000
2.000+002	9.0476-003	9.8892-002	1.1874-003	6.9839-001	1.0681-001	1.8342+000
2.100+002	7.8270-003	8.2093-002	9.6706-004	7.0766-001	1.1489-001	1.8183+000
2.200+002	6.7957-003	6.7748-002	7.8998-004	7.1129-001	1.2057-001	1.8041+000
2.300+002	5.9233-003	5.5623-002	6.4645-004	7.1031-001	1.2627-001	1.7913+000
2.400+002	5.1839-003	4.5462-002	5.2945-004	7.0563-001	1.3121-001	1.7799+000
2.500+002	4.5552-003	3.7020-002	4.3376-004	6.9803-001	1.3545-001	1.7697+000
2.600+002	4.0190-003	3.0063-002	3.5546-004	6.8815-001	1.3903-001	1.7605+000
2.700+002	3.5599-003	2.4385-002	2.9155-004	6.7657-001	1.4200-001	1.7522+000
2.800+002	3.1653-003	1.9801-002	2.3972-004	6.6375-001	1.4441-001	1.7447+000
2.900+002	2.8248-003	1.6152-002	1.9816-004	6.5007-001	1.4631-001	1.7379+000
3.000+002	2.5297-003	1.3299-002	1.6542-004	6.3587-001	1.4774-001	1.7316+000
3.100+002	2.2729-003	1.1117-002	1.4025-004	6.2140-001	1.4875-001	1.7257+000
3.200+002	2.0485-003	9.4959-003	1.2158-004	6.0690-001	1.4938-001	1.7202+000
3.300+002	1.8517-003	8.3329-003	1.0836-004	5.9254-001	1.4969-001	1.7150+000
3.400+002	1.6783-003	7.5340-003	9.9635-005	5.7845-001	1.4973-001	1.7100+000
3.500+002	1.5251-003	7.0153-003	9.4490-005	5.6475-001	1.4956-001	1.7052+000
3.600+002	1.3891-003	6.7056-003	9.2121-005	5.5149-001	1.4922-001	1.7004+000
3.700+002	1.2681-003	6.5471-003	9.1846-005	5.3872-001	1.4876-001	1.6957+000
3.800+002	1.1600-003	6.4953-003	9.3119-005	5.2647-001	1.4821-001	1.6911+000
3.900+002	1.0631-003	6.5169-003	9.5513-005	5.1475-001	1.4760-001	1.6865+000

82-483

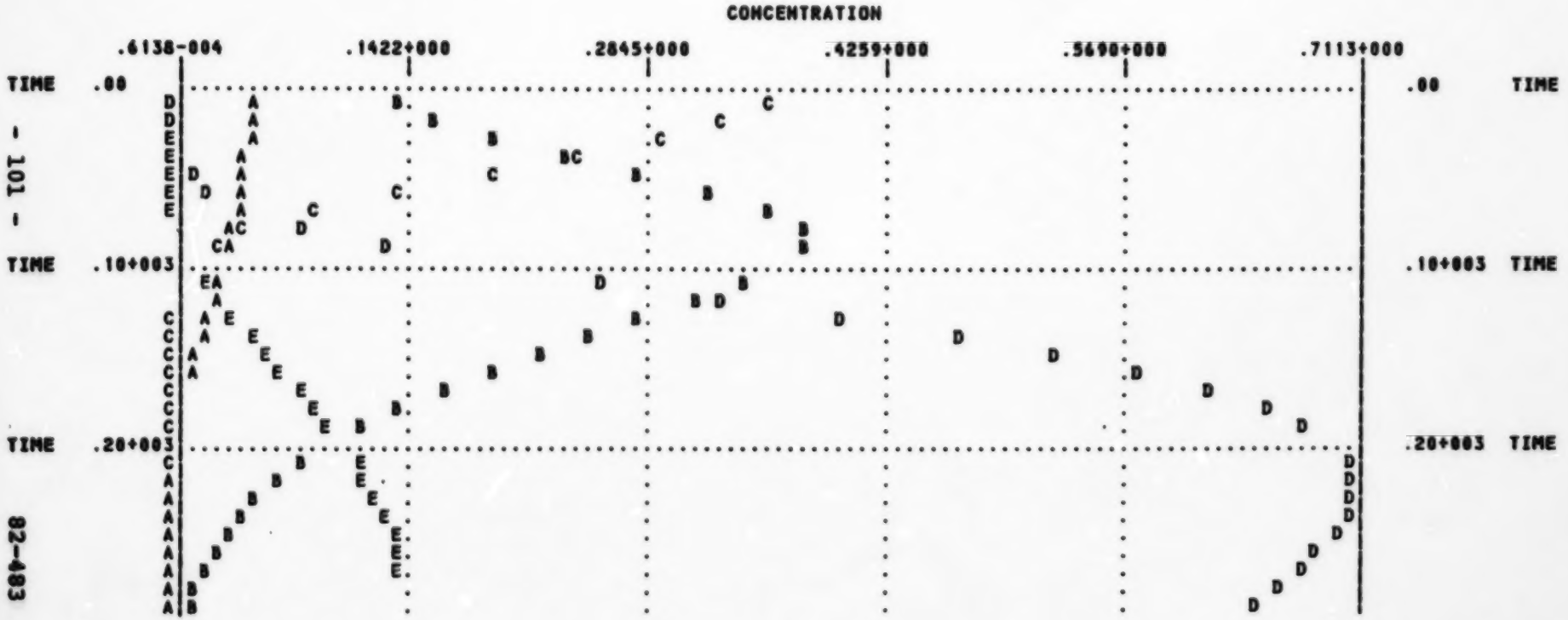
4.000+002 9.7619-004 6.5877-003 9.8702-005 5.0355-001 1.4695-001 1.6818+000

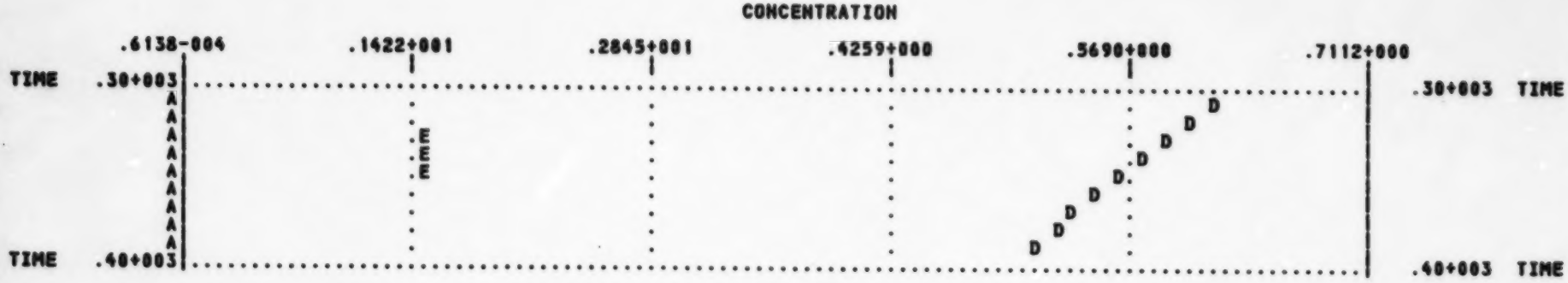
HAVCHM VERIFICATION OF CBM-III , RUN 247

PLOT OF SPECIES

PLOT CODES FOR SPECIES ARE :

A -> OLE B -> NO2 C -> NO D -> O3 E -> PAN

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.1422+001
.2845+001
.4259+000
.5690+000
.7112+000
TIME .30+003
TIME .40+003
.30+003 TIME
.40+003 TIME

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Divide fault occurred: was not checked by program.

Floating point underflow occurred: was not checked by program.

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APPENDIX B

The validation simulation of the chemical reactions which occur in a NO_x-hydrocarbon-SO_2 filled smog chamber are described. The experimental data were obtained from smog chamber experiments conducted by D.F. Miller/24/. For a list of the photolysis rate constants used in the simulation runs and the chamber dependent reactions see Appendix A. The initial NO_x-hydrocarbon-SO_2 concentrations are listed in Table B.1. The hydrocarbon group concentrations as entered into the HAVCHM computer program are listed in Table B.2. A copy of the HAVCHM computer printout including the reaction list, initial concentrations, reaction rate constants and a table of species concentration as a function of time, follows. A summary and comparison of the smog chamber experimental results and the results obtained with the photochemical model are presented in Table B.3.

TABLE B.1

INITIAL HYDROCARBON/NO_x/SO_2 CONCENTRATION DATA

Reactant	Concentration, ppm
Acetylene	0.468
Ethylene	0.450
Propylene	0.118
trans-2-Butene	0.113
2-Methyl-2-Butene	0.030
Ethane	0.234
Propane	0.104
n-Butane	0.265
2-Methylpropane	0.073
n-Pentane	0.116
2-Methylbutane	0.230
2-Methylpentane	0.153
Benzene	0.096
Toluene	0.199
m-Xylene	0.206
p-Ethyltoluene	0.067
1,2,4-Trimethylbenzene	0.044
CO	15
SO_2	0.100
NO	0.252
NO_2	0.052

TABLE B.2

HYDROCARBON GROUP CONCENTRATIONS

Hydrocarbon Group	Concentration (ppm)
OLE	0.118
PAR	5.53
ARO	0.516
CARB	0.286
ETH	0.45

TABLE B.3

A COMPARISON OF THE EXPERIMENTAL RESULTS OF THE SMOG CHAMBER STUDIES WITH THE RESULTS CALCULATED USING THE PHOTOCHEMICAL MODEL [a]

Smog Chamber		Photochemical Model
$[NO_2]_{max}$ (ppm)	0.26	0.24
at time (min)	25	40
NO_2 rate (ppb min^{-1})	8.5	4.8
$[O_3]_{max}$ (ppm)	0.49	0.64
at time (min)	95	140
SO_2 oxidation rate (%h^{-1})	7.5	2
SO_2 conversion (%)	6.7	3
Sulfur aerosol [b] ($\mu g\ m^{-3}$)	36	16.2

a Smog chamber experimental values have been corrected for chamber dilution.

b Mass concentration of sulfate aerosol at 6 h assuming that all of the sulfate is $(NH_4)_2SO_4$ with density of 1.77 g cm^{-3}.

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ERROR TEST CONSTANT FOR DIFSUB 1.000-008
MINIMUM STEP SIZE 1.000-012
MAXIMUM STEP SIZE ..... 1.500+001
UPPER TIME LIMIT TO INTEGRATE ..... 4.000+002

...FIRST 0 MEMBERS OF SPECIES LIST ARE PRINTED OUT AFTER EACH 0 ITERATIONS

...ONLY 7 SPECIES ARE TO BE PRINTED ON PREDEFINED TIME INTERVALS

...DIFSUB METHOD IS 2

...OUTPUT REQUESTED EVERY 1.000+001 TIME UNITS FOR THE FOLLOWING SPECIES :
SO2 OLE NO2 NO O3 PAN PAR

1. REACTION LIST

	1	NO2	+	+	-> NO	+ O	+
	2	O	+	+	-> O3	+	+
	3	NO	+ O3	+	-> NO2	+	+
	4	NO2	+ O3	+	-> NO3	+	+
	5	NO2	+ O	+	-> NO	+	+
	6	OH	+ O3	+	-> HO2	+	+
	7	HO2	+ O3	+	-> OH	+	+
	8	OH	+ NO2	+	-> HNO3	+	+
	9	OH	+ CO	+	-> HO2	+ CO2	+
	10	NO	+ NO	+	-> NO2	+ NO2	+
	11	NO	+ NO3	+	-> NO2	+ NO2	+
	12	NO2	+ NO3	+ H2O	-> HNO3	+ HNO3	+
	13	NO	+ HO2	+	-> NO2	+ OH	+
	14	HO2	+ HO2	+	-> H2O2	+	+
	15	X	+ PAR	+	-> SP	+	+
	16	OH	+ PAR	+	-> MEO2	+ H2O	+

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17	O	+ OLE	+	-> MEO2	+ ACO3	+ X
18	O	+ OLE	+	-> CARB	+ PAR	+
19	OH	+ OLE	+	-> RAO2	+	+
20	O3	+ OLE	+	-> CARB	+ CRIG	+
21	OLE	+ O3	+	-> CARB	+ MCRG	+ X
22	ETH	+ O	+	-> MEO2	+ HO2	+ CO
23	ETH	+ O	+	-> CARB	+ PAR	+
24	OH	+ ETH	+	-> RBO2	+	+
25	O3	+ ETH	+	-> CARB	+ CRIG	+
26	NO	+ ACO3	+	-> NO2	+ MEO2	+
27	NO	+ RBO2	+	-> A1	+ HO2	+ CARB
28	NO	+ RAO2	+	-> A1	+ HO2	+ CARB
29	NO	+ MEO2	+	-> A1	+ MEO2	+ X
29A	A1	+	+	-> CARB	+ NO2	+
30	NO	+ MEO2	+	-> NO2	+ CARB	+ HO2
31	NO	+ MEO2	+	-> NRAT	+	+
32	O3	+ RBO2	+	-> CARB	+ HO2	+ CARB
33	O3	+ RAO2	+	-> CARB	+ HO2	+ CARB
34	OH	+ CARB	+	-> CRO2	+ X	+
35	OH	+ CARB	+	-> HO2	+ CO	+
36	OH	+ CARB	+	-> ACO3	+ X	+
37	CARB	+	+	-> H2	+ CO	+
38	CARB	+	+	-> HO2	+ HO2	+ CO
38A	CARB	+	+	-> MEO2	+ MEO2	+ A2
38B	A2	+	+	-> CO	+ X	+ X
39	HO2	+ ACO3	+	-> PAN	+	+
40	PAN	+	+	-> ACO3	+ HO2	+
41	HO2	+ ACO3	+	-> SP	+	+

42	HO2	+	ME02	+	->	SP	+		+
43	NO	+	CRIG	+	->	NO2	+	CARB	+
44	NO2	+	CRIG	+	->	NO3	+	CARB	+
45	CARB	+	CRIG	+	->	OZNID	+		+
46	NO	+	MCRG	+	->	NO2	+	CARB	+ PAR
47	NO2	+	MCRG	+	->	NO3	+	CARB	+ PAR
48	CARB	+	MCRG	+	->	OZNID	+		+
49	CRIG	+		+	->	CO	+	H2O	+
50	CRIG	+		+	->	SP	+		+
51	CRIG	+		+	->	HO2	+	HO2	+ CO
52	MCRG	+		+	->	SP	+		+
53	MCRG	+		+	->	ME02	+	OH	+ CO
54	MCRG	+		+	->	ME02	+	HO2	+
55	MCRG	+		+	->	CARB	+	HO2	+ A3
55A	A3	+		+	->	CO	+	HO2	+
56	OH	+	ARO	+	->	RARO	+	H2O	+
57	OH	+	ARO	+	->	HO2	+	OPEN	+
58	NO	+	RARO	+	->	NO2	+	PHEN	+ HO2
59	OPEN	+	NO	+	->	NO2	+	DCRB	+ A4
59A	A4	+		+	->	X	+	APRC	+
60	APRC	+		+	->	DCRB	+	CARB	+ CO
61	APRC	+		+	->	CARB	+	CO	+ A5
61A	A5	+		+	->	CARB	+	CO	+
62	PHEN	+	NO3	+	->	PHO	+	HNO3	+
63	PHO	+	NO2	+	->	NPHN	+		+
64	PHO	+	HO2	+	->	PHEN	+		+
65	OPEN	+	O3	+	->	DCRB	+	X	+ APRC
66	OH	+	PHEN	+	->	A6	+	HO2	+ APRC
66A	A6	+		+	->	PAR	+	CARB	+

67	DCRB	+	+	-> HO2	+ ACO3	+ CO
67A	DCRB	+	+	-> MEO2	+ HO2	+ A7
67B	A7	+	+	-> CO	+ CO	+
68	PHEN	+ OH	+	-> PHO	+	+
69	CRO2	+ NO	+	-> NO2	+ HO2	+ DCRB
70	HONO	+	+	-> OH	+ NO	+
71	OH	+ NO	+	-> HONO	+	+
72	O3	+	+	-> O1D	+	+
73	O1D	+	+	-> O	+	+
74	O1D	+ H2O	+	-> OH	+ OH	+
75	SO2	+ OH	+	-> SULF	+	+
76	O3	+	+	-> LOSS	+	+
77	NO2	+	+	-> LOSS	+	+

2. SPECIES LABELS READ AS INPUT

NO2	NO	O	O3	H2O	OH	NO3	HO2	HNO3	CO
CO2	H2O2	X	PAR	MEO2	OLE	ACO3	CARB	RAO2	CRIG
MCRG	ETH	RBO2	CRO2	H2	NRAT	PAN	SP	OZNID	ARO
RARO	OPEN	PHEN	DCRB	APRC	PHO	NPHN	HONO	O1D	A1
A2	A3	A4	A5	A6	A7	SO2	SULF	LOSS	

NUMBER OF REACTIONS 86
NUMBER OF SPECIES 49
NUMBER OF SPECIES VARIED 49

3. INITIAL CONCENTRATIONS

NO2	5.2000-002
NO	2.5200-001
O	.0000
O3	.0000
H2O	.0000
OH	.0000
NO3	.0000
HO2	.0000
HNO3	.0000
CO	1.5000+001
CO2	.0000
H2O2	.0000
X	.0000
PAR	5.5300+000
MEO2	.0000

OLE	1.1800-001
ACO3	.0000
CARB	2.7800-001
RAO2	.0000
CRIG	.0000
MCRG	.0000
ETH	4.5300-001
RBO2	.0000
CRO2	.0000
H2	.0000
HRAT	.0000
PAN	.0000
SP	.0000
OZNID	.0000
ARO	5.1600-001
RARO	.0000
OPEN	.0000
PHEN	.0000
DCRB	.0000
APRC	.0000
PHO	.0000
NPHN	.0000
HONO	.0000
O1D	.0000
A1	.0000
A2	.0000
A3	.0000
A4	.0000
A5	.0000
A6	.0000
A7	.0000
SO2	1.0000-001
SULF	.0000
LOSS	.0000

4. REACTION RATE CONSTANTS

1	3.0000-001
2	4.4000+006
3	2.6600+001
4	4.8000-002
5	1.3000+004
6	1.0000+002
7	2.4000+000
8	1.6000+004
9	4.4000+002
10	1.5000-004
11	2.8000+004
12	1.7000-003
13	1.2000+004
14	1.5000+004
15	1.0000+005
16	1.3000+003
17	2.7000+003
18	2.7000+003
19	3.7000+004

20	8.0000-003
21	8.0000+002
22	6.0000+002
23	6-.2400D+004
24	2.4000-003
25	2.0400+004
26	1-.2000+004
27	1-.2000+003
28	3-.8000+006
29	3-.8000+003
29A	7.7000+002
30	5.0000+002
31	5.0000+002
32	2-.0000+003
33	1-.0000+003
34	7.0000+003
35	6-.9900D-004
36	2.5300-004
37	1.2700D+006
38	1-.0000+003
38A	7.0000-002
38B	2-.5000+003
39	9-.2000+004
40	8-.6000+003
41	2-.2000+004
42	2-.2000+003
43	8.0000+002
44	6.7000+002
45	2.4000+001
46	9-.5000+002
47	3.4000+002
48	4.2500+001
49	8-.0000+006
50	1-.0000+003
51	6-.4500+004
52	4-.0000+003
53	6-.0000+006
54	1-.0000+004
55	1-.0000+004
55A	1-.0000+006
56	5.0000+003
57	4.0000+004
58	5.0000+001
59	4.0000+004
59A	3.0000+006
60	1-.7500-003
61	6.7500-003
61A	1.0000+006
62	
63	
64	
65	
66	
66A	
67	
67A	
67R	

68	1.0000+004
69	1.2000+004
70	1.8000-002
71	9.7700+003
72	.0000
73	4.4400+010
74	3.4000+005
75	1.7700+003
76	1.6000-003
77	1.6000-003

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TIME - CONCENTRATION REPORT

TIME	SO2	OLE	NO2	NO	O3	PAN	PAR
.000	1.0000-001	1.1800-001	5.2000-002	2.5200-001	.0000	.0000	5.5300+000
1.000+001	9.9871-002	1.1475-001	1.0121-001	1.9850-001	5.6293-003	2.7332-004	5.5136+000
2.000+001	9.9660-002	1.0956-001	1.7698-001	1.1445-001	1.6707-002	1.4503-003	5.4872+000
3.000+001	9.9396-002	1.0303-001	2.3745-001	4.0481-002	5.8528-002	4.7627-003	5.4540+000
4.000+001	9.9095-002	9.5009-002	2.4357-001	1.4105-002	1.5677-001	1.0912-002	5.4160+000
5.000+001	9.8764-002	8.5519-002	2.2024-001	6.9282-003	2.7282-001	1.9535-002	5.3734+000
6.000+001	9.8442-002	7.5775-002	1.8588-001	4.1244-003	3.7444-001	2.9656-002	5.3305+000
7.000+001	9.8162-002	6.6760-002	1.5333-001	2.7517-003	4.5337-001	4.0146-002	5.2913+000
8.000+001	9.7929-002	5.8757-002	1.2782-001	2.0021-003	5.1289-001	5.0316-002	5.2571+000
9.000+001	9.7736-002	5.1727-002	1.0757-001	1.5417-003	5.5713-001	5.9894-002	5.2274+000
1.000+002	9.7576-002	4.5577-002	9.0527-002	1.2228-003	5.8922-001	6.8766-002	5.2015+000
1.100+002	9.7442-002	4.0214-002	7.5903-002	9.8541-004	6.1166-001	7.6876-002	5.1790+000
1.200+002	9.7330-002	3.5546-002	6.3312-002	8.0104-004	6.2641-001	8.4208-002	5.1593+000
1.300+002	9.7237-002	3.1488-002	5.2481-002	6.5377-004	6.3502-001	9.0766-002	5.1421+000
1.400+002	9.7159-002	2.7961-002	4.3194-002	5.3385-004	6.3869-001	9.6573-002	5.1271+000
1.500+002	9.7095-002	2.4893-002	3.5270-002	4.3496-004	6.3841-001	1.0166-001	5.1140+000
1.600+002	9.7042-002	2.2222-002	2.8554-002	3.5284-004	6.3499-001	1.0606-001	5.1025+000
1.700+002	9.6998-002	1.9892-002	2.2913-002	2.8454-004	6.2908-001	1.0981-001	5.0923+000
1.800+002	9.6961-002	1.7857-002	1.8233-002	2.2798-004	6.2123-001	1.1295-001	5.0835+000
1.900+002	9.6932-002	1.6074-002	1.4413-002	1.8163-004	6.1193-001	1.1551-001	5.0756+000
2.000+002	9.6907-002	1.4509-002	1.1365-002	1.4439-004	6.0156-001	1.1753-001	5.0686+000
2.100+002	9.6887-002	1.3131-002	9.0064-003	1.1535-004	5.9049-001	1.1904-001	5.0623+000
2.200+002	9.6869-002	1.1914-002	7.2579-003	9.3709-005	5.7900-001	1.2007-001	5.0566+000
2.300+002	9.6855-002	1.0835-002	6.0324-003	7.8584-005	5.6736-001	1.2068-001	5.0514+000
2.400+002	9.6842-002	9.8763-003	5.2345-003	6.8946-005	5.5576-001	1.2094-001	5.0465+000
2.500+002	9.6830-002	9.0214-003	4.7648-003	6.3659-005	5.4437-001	1.2091-001	5.0419+000
2.600+002	9.6819-002	8.2567-003	4.5318-003	6.1630-005	5.3329-001	1.2068-001	5.0374+000
2.700+002	9.6809-002	7.5708-003	4.4612-003	6.1937-005	5.2258-001	1.2029-001	5.0331+000
2.800+002	9.6799-002	6.9538-003	4.4982-003	6.3877-005	5.1228-001	1.1981-001	5.0288+000
2.900+002	9.6789-002	6.3976-003	4.6045-003	6.6944-005	5.0241-001	1.1925-001	5.0245+000
3.000+002	9.6778-002	5.8948-003	4.7543-003	7.0778-005	4.9296-001	1.1865-001	5.0202+000
3.100+002	9.6768-002	5.4395-003	4.9300-003	7.5124-005	4.8393-001	1.1801-001	5.0160+000
3.200+002	9.6758-002	5.0262-003	5.1194-003	7.9793-005	4.7533-001	1.1735-001	5.0117+000
3.300+002	9.6747-002	4.6503-003	5.3140-003	8.4644-005	4.6712-001	1.1667-001	5.0074+000
3.400+002	9.6736-002	4.3078-003	5.5078-003	8.9570-005	4.5930-001	1.1598-001	5.0032+000
3.500+002	9.6725-002	3.9953-003	5.6967-003	9.4486-005	4.5186-001	1.1529-001	4.9988+000
3.600+002	9.6713-002	3.7095-003	5.8774-003	9.9326-005	4.4477-001	1.1460-001	4.9945+000
3.700+002	9.6702-002	3.4477-003	6.0480-003	1.0404-004	4.3802-001	1.1391-001	4.9901+000
3.800+002	9.6690-002	3.2077-003	6.2070-003	1.0858-004	4.3159-001	1.1321-001	4.9857+000
3.900+002	9.6677-002	2.9871-003	6.3535-003	1.1292-004	4.2547-001	1.1252-001	4.9813+000

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4.000+002 9.6665-002 2.7843-003 6.4870-003 1.1704-004 4.1964-001 1.1184-001 4.9769+000

APPENDIX C

TYPICAL HYDROCARBON COMPOSITION AT RURAL AND URBAN SITES IN THE SURE REGION/25/

(Selected averages for 0700-0900, July 1976)

Compound	Urban Area	Rural Area
C_2H_6	5.9 ppb	4.1 ppb
C_2H_4	----[a]	8.7
C_3H_8	5.2	4.3
C_2H_2	7.5	3.3
Iso C_4H_{10}	2.5	1.4
N-C_4H_{10}	11.0	5.5
C_3H_6	5.6	0.7
C_4H_8[b]	--	--
Iso-C_5H_{12}	8.9	3.4
N-C_5H_{12}	3.7	2.0
C_5H_{10}[b]	--	--
N-C_6H_{14}	2.6	1.0
N-C_7H_{16}	0.7	0.4
Toluene	9.9	2.1
N-C_8H_{18}	0.8	0.2
E-C_6H_5	2.7	1.3
M-XYLENE	8.4	3.8
O-XYLENE	2.4	1.0

[a] Uncertain because of interference from C_2H_4/O_3 chemiluminescent O_3 monitor.

[b] C_4 and C_5 olefins typically observed at suburban and urban sites in range of 0.2-2 ppb.